SYNTHESIS OF NEW CROSS-LINKED MELAMINE BASED POLYAMINES IMPREGNATED CARBON NANOTUBE COMPOSITES FOR TOXIC METAL ION REMOVAL

BY

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Dedication

I dedicate this research work to my God and Creator for his protection, providence and mercy. I give him all the glory for giving me the grace to manifest his desires for me. He is the sole hinge on which my life rest on. In fact, He is the essence of my existence. I also want to dedicate this piece to my parents Mr Emmanuel and Mrs Janet Adelabu for being the marshal behind my success.

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LIST OF ABBREVIATIONS

CMA	:	Carbon nanotubes Melamine Alkyldiamine
CNT	:	Carbon nanotubes
DMF	:	N,N-Dimethyl formamide
FT-IR	:	Fourier Transform Infrared Spectroscopy
NMR	:	Nuclear Magnetic Resonance spectroscopy

ABSTRACT

Full Name : Adelabu Isaiah Olabisi

Thesis Title : [Synthesis of new cross-linked Melamine based polyamines impregnated Carbon nanotube composites for toxic metal ion removal from waste water]

Major Field : [Chemistry]

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Novel series of carbon nanotubes functionalized polymers were synthesized via a single step one pot polycondensation reaction of melamine, paraformaldehyde and alkyldiamines at optimized reaction conditions in the presence of N, N-Dimethyl formamide as solvent. Highly reactive chlorinated carbon nanotubes synthesized by reacting acidified CNT and thionyl chloride was used.. The crystal morphology, particle size distribution, molecular structures and overall properties of the new series of polymers were characterized using Raman Spectroscopy, C H N S elemental analyzer, Fourier transform infrared spectroscopy(FT-IR), ^{13}C Nuclear magnetic resonance (NMR), X-ray diffraction experiments (XRD), Scanning electron microscopy(SEM-EDX), BET surface area analysis and Thermogravimetic analysis(TGA) . A comprehensive design was set up in order to evaluate the effects of pH, temperature, dosage, metal ion initial concentrations and contact time on the ability of the new series of functionalized polymers for toxic ion removal. The mechanism and mode of adsorption was investigated using Langmuir, freundlich and langragian pseudo second order isotherm model with well fitted correlation between results . After the polymer composites have been

successfully synthesized and characterized, they were thereupon used for toxic metal ions (Lead, Cadmium, Arsenic, Nickel, Zinc, Chromium, Mercury.) removal from prepared toxic solutions and real waste water samples. An overall removal efficiency of about 99% was achieved.

ملخص الرسالة

الاسم الكامل : آيـ زيـ ا أولاب يـ سي عادل أبـ و

عنوان الرسالة: ن ت حـ ضـ ير بـ ول يمرات بـ ول ياميـ ين جديـ دة من الـ مـ يلامـ ين عـ لى أذ ابـ يب الـ كربـ و
لإزالة أيونات المعادن السامة من مياه الصرف الصحي

التخصص: كيمياء

تاريخ الدرجة العلمية : وياام 2016

تم تصنيع نوع جديد من البوليمرات عن طريق دمج أنابيب نانونية كربونية على سلسلة من البوليمرات مصنعة عن طريق التفاعيل التكاثفي باستخدام ثلاث مواد مختلفة وهي عبارة عن الكينات ثنائية الأمين، فولمالديهيد و مادة الميلامين. للحصول على أفضل نتيجة للتفاعل تم استخدام ثنائي المثثيل فورمأميد كمذيب. تم الحصول على أسيل كلوريد أنابيب الكاربون النانونية عن طريق تفاعل أنابيب كاربون نانونية حمضية مع مادة الثيونيل كلوريد. تم توصيف المواد باستخدام العديد من الأجهزة. قد تم الحصول على خاصية التبلور، الحجم الجزيئي والتركيب الجزيئي للمواد باستخدام جهاز رامان الطيفي، جهاز الأشعة تحت الحمراء، جهاز الرنين النووي المغناطيسي، جهاز الحيود السيني والمجهر الماسح الالكتروني. الجهاز الوزني الحراري قد تم استخدامه لمعرفة الاستقرار الحراري للمواد. قدم تم أداء تجارب ادمصاص للمواد الجديدة في ظروف متعددة من الحرارة، الأس الهيدروجيني، الجرعات، التركيز الابتدائي للمعدن ومدة عملية الادمصاص. لمعرفة ماهية عملية الادمصاص، لقد تم استخدام متساويات حرارة مثل لانغويمر وفريندلش. لاحقا، المواد الجديدة تم تجريبها في عملية إدمصاص المعادن الثقيلة من مياه الصرف.

CHAPTER 1

INTRODUCTION

The increasing demand for high quality drinking and industrial water has necessitated the enforcement of stringent regulations to guide the use of water in the domestic, commercial and industrial context. It's expected that in the years to come, most water plants will have to brace up and improve their water treatment technologies to achieve optimum quality, low cost and little or no environmental side effects[1, 2]. The current trends of water treatment technologies involve processes such as filtration, ion exchange mechanisms, coagulation, sedimentation, disinfection, flocculation and adsorption. Of all these current technologies, adsorption technologies which employs the usage of versatile adsorbents have proven to be a very good option as a process suitable for removing low level concentration of toxic heavy metal in a single step process effectively and efficiently.

Several adsorbents have been employed to achieve this technology. Of all these, the use of polymers have significantly attracted more appraisal due to the regenerative potential. As a further modification, polymeric matrixes have been adjudged in some applications to show improved properties based on the incorporation between the inorganic-organic component's properties to achieve a comprehensive overall sorption activity. With the emergence of nanotechnology and versatile nanomaterials, there has been subsequent

introduction of nanomaterials into the polymer matrixes to yield composites combining the properties of the later and former to achieve a laudable adsorption capacity. The carbon nanotubes and nanomaterials applied as modifiers improve the polymeric properties, making the polymer a better adsorbent. Carbon nanotubes and graphenes are known for their extremely high surface area, better mechanical properties and thermal strength. With all these advantages, there is absolute need to synthesize novel materials that synergize both the properties of inorganic and organic ends while achieving a relatively high sorption potential [3, 4].

In this research, studies will be examined on the combination of the properties of carbon nanotubes and those of the polymers in order to achieve the target application. Then, a series of new cross-linked polymers will be synthesized by the polycondensation reaction of modified melamine, various diaminohexane and paraformaldehyde.

The new polymers will be designed, synthesized and optimized in a one-step polymerization reaction, intended to be used for commercial and industrial wastewater treatment. After the polymer composites have been successfully synthesized, they will be characterized using various characterization techniques, elemental analysis and imaging techniques. The synthesized cross-linked polymer composites will be tested for their efficiency in the removal of toxic metal ions from aqueous solutions in batch and for large waste water sample.

The Adsorption efficiency of the synthesized polyamines will be evaluated under various conditions like:

1- Effect of pH.

2- Effect of metal ion initial concentration.

3- Effect of temperature.

4-Effect of contact time

5- Effect of polymer composite dosage

At the second stage, the data collected will be subjected to different kinetic and thermodynamic isotherm models, in order to investigate the adsorption potential and mechanism of metal ion uptake.

The final stage in this study, the polymeric materials (carbon nanotubes, paraformaldehyde, diaminohexane and melamine) will be employed in the treatment of wastewater samples that will be collected from different water treatment plants. These novel polymer composites will be tested for sorption of toxic metal ions from sample water/ wastewater. This research project will make a meaningful addition to the science of environmental remediation, advanced materials, water treatment areas and protection both for the biotic and abiotic components of the ecosystem. It is important for the industrial, domestic and environmental vantage points.

1.1 Research problem

The increasing demands for efficient adsorbents and materials have necessitated intense research and synthesis in this field. Over the past few decades, attentions have been driven towards the synthesis of affordable, selective, sensitive and efficient materials to

achieve this purpose. This research work is geared at the synthesis of new polymeric materials for the removal of toxic heavy metals such as lead, mercury, arsenic e.t.c selectively and effectively. The synthesized polymers as well as its modified resultant polymers will be a new class of materials for these applications. Characterization and examination of the efficiency will be done under various conditions as earlier stated and this will be compared to the other results from selected literature of high impact.

1.2 Expected Outcome

At the completion of this research project, the following results are expected;

- New and reliable polymers obtained from CNT-melamine, alkyldiamines and paraformaldehyde will be developed for effective heavy metals removal.
- Application of the polymeric materials for selective heavy metals removal.
- Application for water and real waste water samples at optimized conditions.
- Opening a new door to new precursors for synthesizing functionalized polymeric materials.

1.3 Literature review

Heavy metals pollution in the aquatic system and water bodies has been a major threat to human and environmental safety. In recent years, attentions have been drawn to the high toxic potentials of these heavy metals because they are non-biodegradable [5, 6]. Heavy metals are released into the aquatic systems as a result of human day to day activities

arising from domestic to industrial processes. These metals are known to bio accumulate and are therefore introduced into the food chain through contaminated soils and water. Municipal effluent and waste waters are characterized by the presence of heavy metals such as Pb, Cu, Zn, As etc and organic pollutants [5, 7-9]. The uptake and presence of these metals in the human body can result in kidney damages, brain disorders, organic malfunctioning, thyroid gland infections and bone contamination. The main source of these heavy metals in the water are the released effluents from domestic activities, textile mills, metal processing and electroplating industries, electric fuel cells, batteries and pigment industries [10, 11]

1.3.1 Heavy metals and toxicity

Heavy metals are a classified class of highly dense metals having a density of higher than 5g per cubic centimeter as well as a relatively high atomic number. The prevalence and the release of these toxic class of metals can be attributed to the activities of industries ranging from chemical manufacture, batteries production, mining and metallurgy, tannery, paper production and fertilizers manufacture [12, 13] . As a result of this high level of industrial actions, large amount of these non-biodegradable toxic metals tend to accumulate in aquatic organism thereby posing threat to the dependents of the food chain structure. Large amounts of some heavy metals are found in polluted water. These metals may be discharged from agricultural run-off on farmlands, urban run-off, industries e.t.c into surface waters thereby cause pollution. Heavy metals have the affinity for sulphur and other functional groups thus forming toxic complexes when they complexate. They

bind to cell membranes affecting transport process through the cell wall. These heavy metals include: Mercury, Cadmium, Arsenic, Chromium, Copper, Manganese, Nickel, Lead, Iron, Zinc e.t.c. [14, 15]

The advancement in technology has led to high level of industrialization leading to the discharge of effluents containing heavy metals in our environment.

Some of the heavy metals are essential and even found useful when they are at low levels for proper growth of plants and animal nutrition. They become toxic when they are above the required levels and are passed on to man by the food chain processes and their accumulations have adverse effects on plants, animals and even humans[12, 16, 17]. The table below summarizes the tolerable limits of heavy metals of top concern

Table 1.1 US EPA[18] and WHO[19] maximum limits of some heavy metals in drinking water

Heavy metals	WHO provisional guideline value (mg/L)	US EPA maximum contamination limit (mg/L)
Mercury	0.006	0.002
Lead	0.01	0.015
Cadmium	0.003	0.005
Arsenic	0.01	0.01
Nickel	0.07	-
Copper	2	1.3
Zinc	3	5
Chromium	0.05	0.1

Mercury (Hg)

Mercury with the chemical symbol Hg is ranked one of the most dangerous of the heavy metals series. Its toxicity and bioaccumulation coupled with its existence in various states makes it of great health concern. Mercury is released into circulation from metals

processing, fossil fuels, earth sub surfaces and water bodies. They are particularly noted for their high mobility and relative ease of bioaccumulation. When present above a tolerable limit of about 0.006mg/L, they tend to attack the human nervous, reproductive, immune and cardiovascular system; and can also extend damages to the kidney, liver and other vital organs. Their effects are significant both in the short, middle and long run. In the light of this, stringent rules have been put in place by regulatory bodies to mitigate the spread of mercury while keeping its level below the harmful quotients [20-27] .

Lead (Pb)

Another class of toxic metal ions are non-biodegradable lead in various form which find easy route into the human body system. As early as 2000 BC, lead's toxicity was identified and recorded and the extensive use of lead has been attributed to various life threatening ailments. One of the major channel through which lead enters the body is through drinking water and are spread throughout the body through body fluids. When present above the maximum limit, they can lead to kidney diseases, anemia, cancer and mental shortcomings [28-33].

Cadmium (Cd)

Cadmium (Cd) is found in deposits along with other elements. Potentially found to accumulate in the kidney, Cd is very toxic and is regarded as one of the priority contaminants in drinking and waste water. Cadmium finds its sources from cooling towers, plastic industries, metal processing industries and metallurgical operations. Cadmium is also found in cadmium alloyed solar cells and batteries making it more prevalent and easy to enter into circulation [34-41].

Arsenic (As)

Arsenic, a common class of heavy metals is brought into circulation by human and natural means. They are particularly resultants of volcanic weathering, mining, metallurgy and arsenic based insecticides that are released into water streams. According to the report by the National Arsenic occurrence survey, a threatening 5µg/L are present in 10% surface water and 21% ground water. A major reason to be worried about arsenic contamination is linked to its direct attribution to different types of cancer. In addition, it has a direct linkage with internal tumors, bladder and kidney damages e.tc. According to the WHO, when present above a maximum limit of 0.003mg/L it poses a considerable measure of damages [42-49].

Nickel (Ni)

Nickel pollution in waste water stems from industrial actions such as Zinc blasting, alloy manufacture, refining of silver, batteries production etc. It is a special class of non-biodegradable toxic heavy metal with direct linkages to cyanosis, dry cough, lung cancer, nausea and chest pain [50-53].

Copper (Cu)

One of the most common of the heavy metals due to its wide ranges of application in industrial, production and agricultural process. Second to mercury in its toxicity rating when in contact with drinking water. Although, it is important for effective plant and human metabolic activities but when present above a certain tolerable limit it can damage the human system causing convulsions, kidney damages, blood pressure and respiratory disorders [36, 54-57].

Zinc (Zn)

Zinc is released into the environment from one or combination of agricultural activities, intrusion and remobilization of sediments due to activities such as galvanizing, steel works, electroplating and paper production. It plays an important role in many biochemical and metabolic processes however, over concentration can cause anemia, skin irritations, nausea etc [58-61].

Chromium (Cr)

Chromium known as one of the most abundant elements and ranked as the sixth most abundant member of the transition elements. Highly known for its toxicity because of its ability to change oxidation states from +2, +3 to +6 depending on the target bonded atom. Majorly present as ores, they are released into the environment by metal exploration, coating , tanning and chromate preparation. The WHO provisional guidelines state that when present above 0.05mg/L in drinking water, it can cause pulmonary damages, vomiting and kidney damage [62-65].

1.3.2 Metal Removal technologies

Coagulation, ion exchange, adsorption, filtration, sedimentation, precipitation, etc has been employed as technologies for removal of pollutants from water. Of all these, adsorption is recognized to be the best for toxic metals removal [66, 67]. The use of adsorbents made of polymers has gained serious attention, and hyper cross-linked polymers with nitrogen, oxygen modified resins have received particular attention [68]. Hyper-cross-linked resins with mesoporous and microporous nature have been reported to adsorb aniline from aqueous solutions. This removal trend of aniline was reported to follow the pseudo-first order rate equation and the adsorption isotherms were correlated to the Freundlich model [69].

It was reported that cross-linked polymeric material that has been functionalized with formaldehyde carbonyl groups has high adsorption capacity for methyl orange and Rhodamine B with a pattern which fits thesemi-empirical Freundlich isotherm, and obeyed the pseudo second order rate model and intra-particle diffusion as the rate-

limiting step [70].Gurnule et al (2002) researched the ion exchange properties of a salicylic acid-melamine-formaldehyde terpolymer resin for the removal of seven metal ions which are Zn, Ni, Cu, Pb, Co, Fe and Cd ions [71]. Nanotechnology could be a major game changer in enhancing the effectiveness and efficiency of polymeric adsorbents. Incorporating metal oxides materials with polymer matrixes is acknowledged to be a better way of enhancing resins due to their hydrophilic nature [72]. Nanomaterials can be incorporated by coating, doping, impregnation and polymerization; scanning through literatures, various inorganic nanomaterials have been incorporated into different types of polymers [73-75]. The high surface area and mechanical properties of carbon nanotubes and graphenes can be explored in polymeric nanocomposites to improve the effectiveness of resins with high structural strength [76-78]. The applications of carbon nanotubes (CNTs) by incorporating them into polymers to yield polymer composites are of great importance [79].

In view of literatures discussed above, it has been observed that the developments of adsorbents with high sorption potential are achievable using carbon nanotubes and melamine-paraformaldehyde-alkyldiamine adsorbents. In this research, single step polycondensation reaction of carbon nanotubes modified melamine, paraformaldehyde and various alkyldiamines will be employed to synthesize new polymeric adsorbent with an excellent sorption ability which will be used for water treatment operations. This research cuts through the fields of advanced materials, water treatment and adsorption technology; it is expected to play a significant role in achieving excellent enrichment efficiency of the desired polymers

CHAPTER 2

Novel Cross-linked Melamine based Polyamine/CNT composite for waste water treatment

ABSTRACT

A novel series of carbon nanotubes functionalized polymers were synthesized via a single step polycondensation reaction of melamine, paraformaldehyde and 1, 6-diaminohexane at optimized reaction conditions in the presence of N, N-Dimethyl formamide as solvent. Highly reactive chlorinated carbon nanotubes synthesized by reacting acidified CNT and thionyl chloride was used. The pure polymer (MFDH) and the functionalized composites (MFDH1, MFDH2, MFDH3 and MFDH4) having 0.01, 0.02. 0.05 and 0.1% weight of the starting precursors were used. The crystal morphology, particle size distribution, molecular structures and overall properties of the new series of polymers were characterized using Raman Spectroscopy, FT-IR, ^{13}C NMR, X-ray diffraction experiments, SEM, AFM, BET and TGA. A comprehensive design was set up in order to evaluate the effects of pH, temperature, Lead(II) ion initial concentrations and contact time on the ability of the new series of functionalized polymers for Lead(II) ion removal.

2.1 Introduction

Water resources contamination has been an increasing challenge for researchers and scientists. Over the last few decades, this contamination by heavy toxic metals, organic pollutants and hydrocarbons have been under serious investigation in a bid to reduce and

eliminate the side effects tied to the prevalence of these contaminants. It is however not strange that these heavy metals over time have been a serious threat to the domestic and industrial worlds as well as the entire ecosystem [1, 19]. The increasing demand for high quality drinking and industrial water has necessitated the enforcement of stringent regulations to guide the use and processing of water resources. These heavy metals such as mercury, arsenic, lead, cadmium, chromium e.t.c. are characterized by relatively high density and atomic weight; this infers that even at a very minute amount, their toxicity is significant. Of particular importance is the removal of Lead (II) ions (Pb^{2+}) because of its high prevalence and toxicity in water bodies. Lead (II) ions have been directly associated with the disruption of the proper functioning of the Kidney, bones, intestines, liver, nervous and reproductive systems[17, 80]; the adverse effects of Lead (II) ions is not limited to humans only but the also the entire eco-system. Of significant concern is the presence of Lead(II) ions above 10 μg/dL in the blood stream[17]. It is expected that in the years to come, most water plants will brace up and improve their water treatment technologies to achieve optimum quality, low cost and little or no environmental side effects [1, 2, 81]. Having recognized the fact that the process technologies contribute to the heavy contamination index, there is a need to embark on sustainable and efficient technologies to tackle this raising problem. The current trends of water treatment technologies involve processes such as filtration, ion exchange mechanisms, coagulation, reverse osmosis, solvent extraction[82], flotation, sedimentation[83], disinfection and adsorption [19, 67, 84-86] [9, 87]. Of all these treatment technologies, adsorption has been adjudged as one of the best techniques because of ease of manufacture, adsorbent regeneration, eco-friendly nature, cost effectiveness and efficiency [88-90].

For the removal of heavy metals from contaminated aqueous media, fabrication of efficient adsorbent is of paramount importance. Conventional credits have been attributed to polymers with high adsorption potentials and activity. These polymers carry functional groups and active moieties that form complexes with target toxic metal ions by chelation. These moieties include and are not limited to carbonyl, amines and thiocarbamates [9, 91-94]. Melamine-formaldehyde-dietheylenetriaminepentaacetic acid for heavy metals removal was a good illustration of an amine moiety chelating with divalent toxic metal ions to aid removal via adsorption[95]. The combination of the strong covalent bond during melamine-formaldehyde polymerization and the presence of active amine ends make this class of adsorbents excellent [93, 95]. Although this class of adsorbents shows quite unique properties, nevertheless their thermal stability, life span and mechanical strength still pose a threat to researches who desire an adsorbent that can function at a relatively high temperature over a long period of time without losing its efficiency. Therefore, in order to solve this setback, composites based on the incorporation between organic and inorganic components came as a saviour. Carbon nanotubes and graphene oxides which possess excellent mechanical properties, high surface area and thermal stability are recently used as modifiers for reinforcing polymers [3, 4, 96]. This advantage has opened a door for a new class of composites that synergize properties of both organic and inorganic ends while achieving relatively high sorption potential[4]. The combination of the properties of the polycondensation polymers of melamine-formaldehyde-diaminohexane with nanomaterials to form adsorbents composites is a promising research gate to excellent adsorbents with unique properties. This will automatically serve as a rescue to previously synthesize adsorbents that suffered the limitations stated above. In

this study, melamine-formaldehyde-diaminohexane polymer was functionalized with different weight percentage of chlorinated carbon nanotubes (0.01, 0.02. 0.05 and 0.1%) . The adsorptive potential, thermal stability, morphology and interactions have been studied in details. The novelty of this work comes from the interaction and mechanism of reaction between melamine-formaldehyde-diaminohexane polymer and Carbon nanotubes.

2.2 Experimental Section

2.2.1 Materials

Melamine, 1, 6-diaminohexane and paraformaldehyde were supplied by Fluka Chemie AG (Buchs, Switzerland) and were subsequently used as received with further modification. N, N-Dimethyl formamide (DMF), Acetone and Methanol were supplied by Sigma-Aldrich, Germany. All other solvents and reagents employed were standard and of analytical grade.

2.2.2 Chemical analysis, thermal analysis and morphology/surface characterization

Infrared spectra of the composites were analyzed on a Perkin Elmer 16F PC FTIR spectrometer using KBr pellets in the 4000-500 cm^{-1} wavelength region. Micrometrics TriStar III BET surface area Analyzer with Burnauer–Emmett–Teller (BET) N2 method. Elemental analysis was done using a Perkin-Elmer Elemental Analyzer series II Model 2400. Powder X-ray Diffraction pattern for crystal nature was recorded using Rigaku Miniflex II Desktop X-ray Diffractometer with 3^0 and stop angle of 70^0 sampling step

size of 0.03, scan speed 3.00, 30KV and 15mA. Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) analyses of the waste water before and after treatment with composites were done using ICP-MS XSeries-II (Thermo Scientific). Solid state ^{13}C-NMR spectra were taken using Bruker WB-400 spectrometer with a spinning rate of 10 KHz.

2.2.3 Synthesis of Polymer/CNT Composites (MFDH).

One pot in-situ polymerization reaction of melamine (1.9 mmol, 0.24 g), 1, 6-diaminohexane (5.7 mmol, 0.344 g) and paraformaldehyde (11.4 mmol, 0.664) and a specific amount of chlorinated CNT (0.00, 0.01, 0.02, 0.05 and 0.1 wt. %) prepared by reflux of activated Carbon nanotubes (CNT) (5% COOH) in excess thionyl chloride were sonicated in 6ml of DMF in nitrogen inert atmosphere for 30 minutes. The reaction mixture was stirred at 90^{o}C for 24 hours. The product was washed in DMF, distilled water and acetone, and dried at 60^{o}C under vacuum until constant weight achieved (Table 1).

Table 2.1 Polymerization results for the synthesis of CNT-Polymer composites

Product code	%wt. CNT	Yield (%)	Elemental analysis		
			% C	% H	% N
MFDH	-	64.1	68.08	11.78	16.63
MFDH1	0.01	65.3	65.43	12.52	17.03
MFDH2	0.02	69.4	67.62	13.10	17.28
MFDH3	0.05	70.8	68.03	13.35	17.58
MFDH4	0.1	72.4	67.81	13.59	17.10

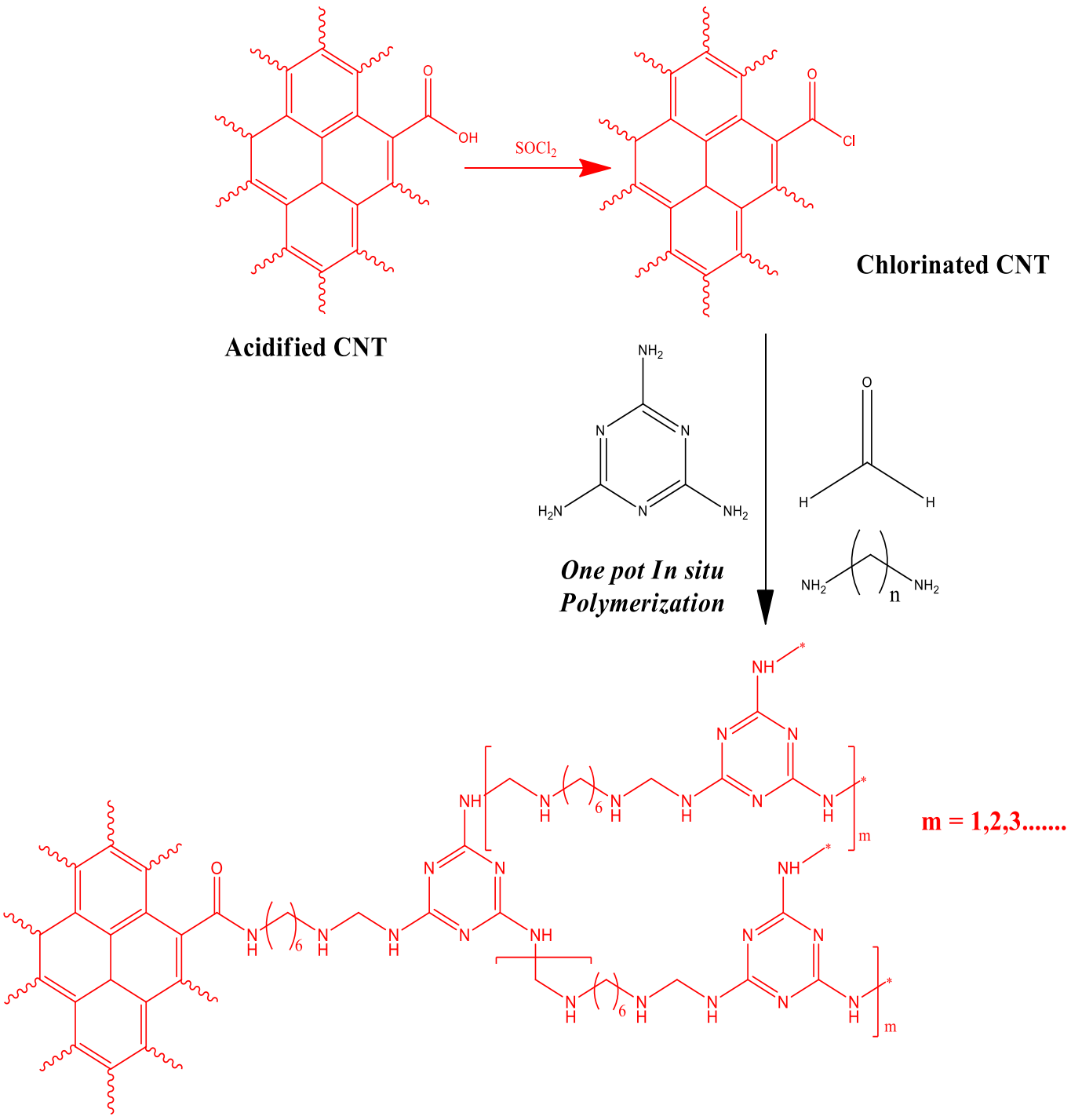
Yield (%) = (product mass/ reactants total mass) × 100%.

% wt. of CNT relative to reactants weight.

2.3 Results and discussion

2.3.1 Synthesis and characterization of polymer composite (MFDH)

The polyamine–CNT composites (scheme 1) were prepared by one pot polycondensation reaction. The synthesized material revealed a distinctive difference in color as the percentage of CNT % increased as shown in figure 2.1.



Scheme 2.1 Reaction scheme for cross linked polymer/composite

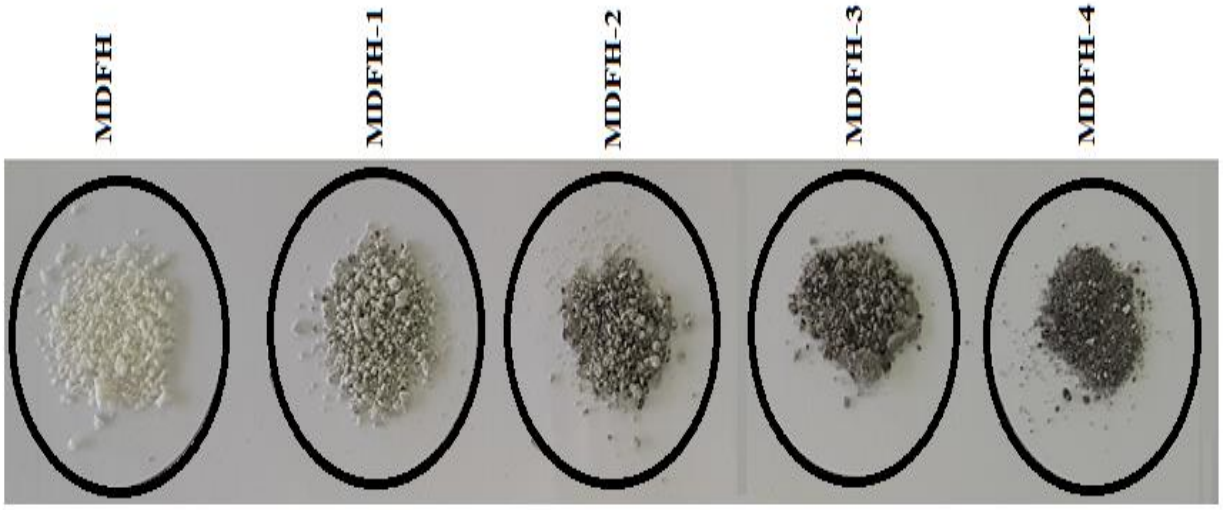


Figure 2.1 Effect of CNT% on the color of polymer/CNT composite.

The polymer composites were characterized using different spectroscopic methods, as the polymer and polymer composites are insoluble in different solvents. The ^{13}C NMR spectra revealed the formation of the proposed polymer structure as shown in Figure 2.2 below, also, as the amount of CNT increased to 0.1 wt.% the CNT material masked the peaks as noise build up in the spectra.

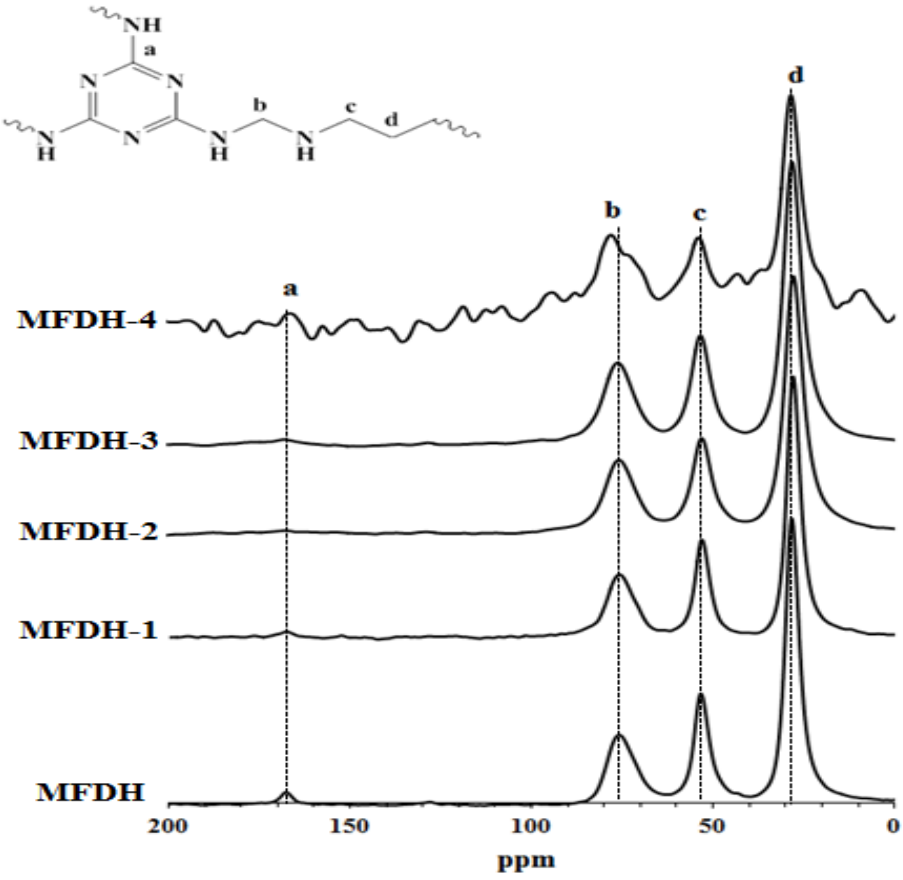


Figure 2.2 ^{13}C-NMR spectra for the synthesized polymer/CNT composites.

FT-IR spectra shown in Figure 2.3 below , reveals the presence of a broad band ~ 3450 cm^{-1} assigned to –NH– and –OH– groups, and a band in MFDH ~3200 cm^{-1} assigned to secondary amine, the peaks ~2960 cm^{-1} assigned to $–CH_2–$ symmetric and asymmetric stretching vibrations. Bands ~1450 to ~1640 cm^{-1} are assigned to –C=N–triazine ring in melamine and the amide –CO(NH-) linkage between CNT and polymeric structure.

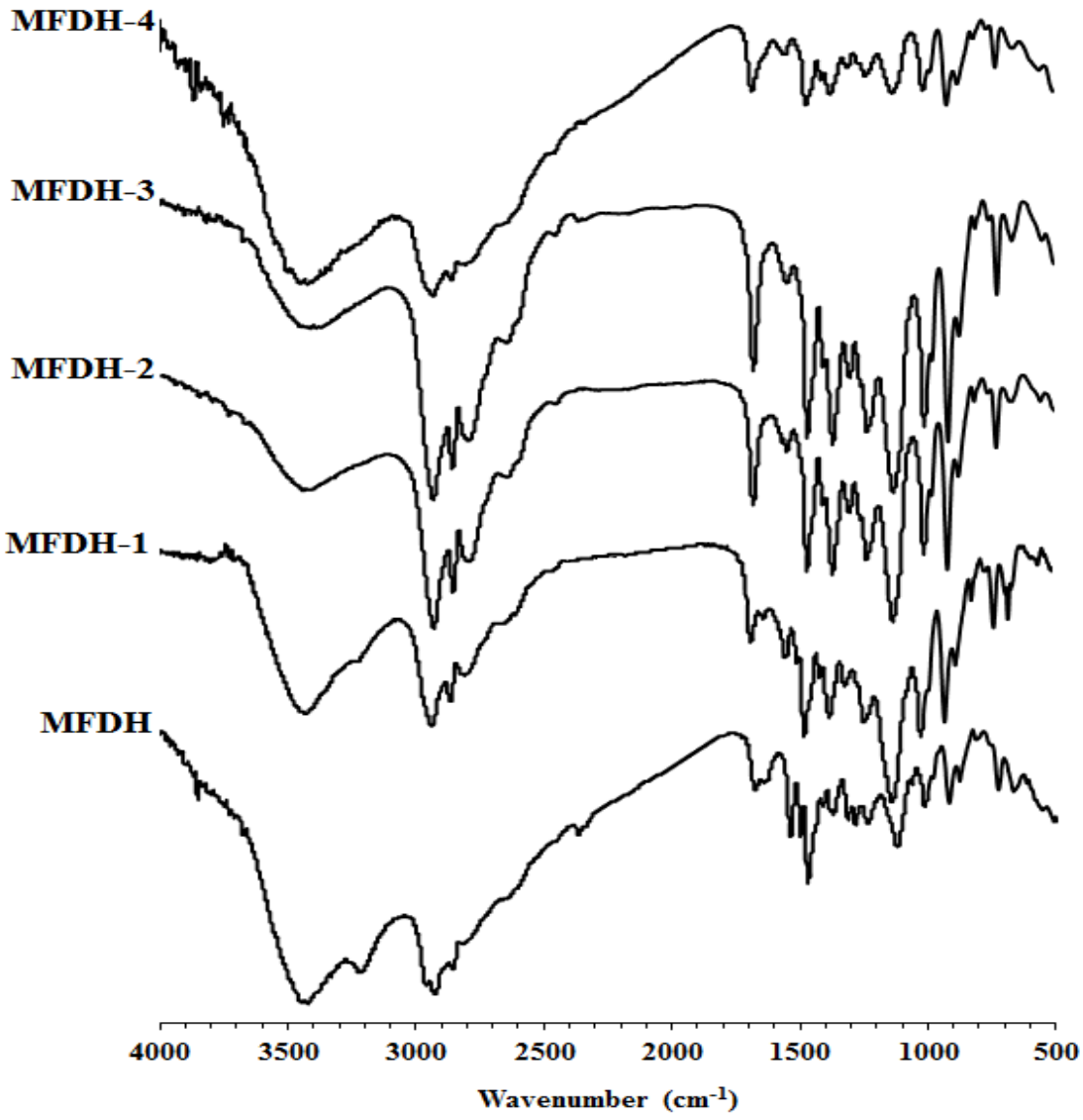


Figure 2.3 FT-IR Spectra for the synthesized polymer composites.

Raman scattering experiments was utilized to detect the CNT bands in the polymer composite. The spectra shown in Figure 2.4 below revealed at ~1600 cm^{-1} an increase in the G-band intensity, which corresponds to the incorporation of CNT with the polymeric material at different weight percentage to form the polymer composite.

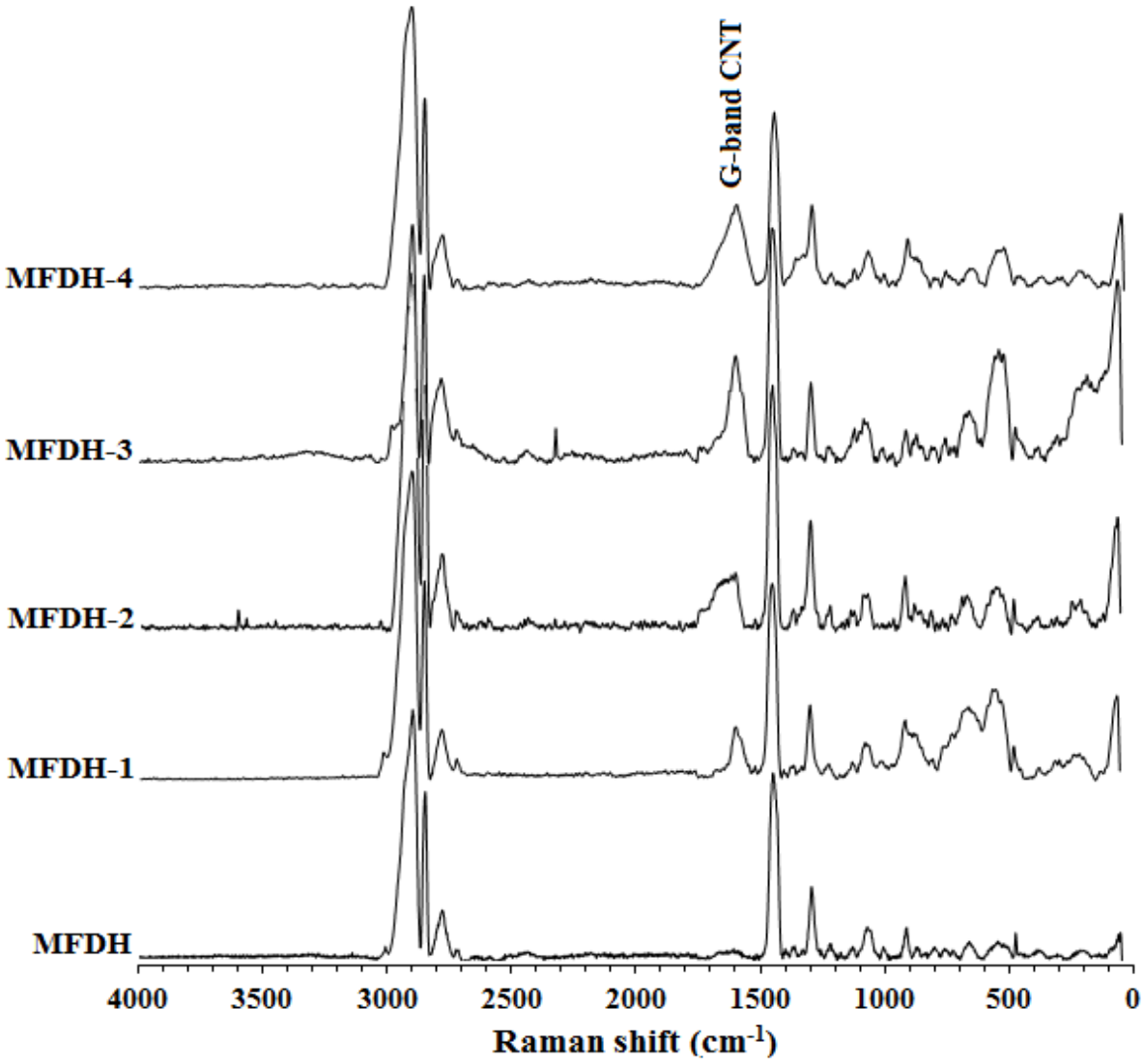


Figure 2.4 Raman Spectra of synthesized polymer composites.

XRD diffraction patterns shown in Figure 2.5 below revealed the decrease in the degree of crystallinity of the synthesized composites as the amount of CNT increased. This could be attributed to the increased disruption of the semi-crystalline order of the synthesized pure melamine based polymer.

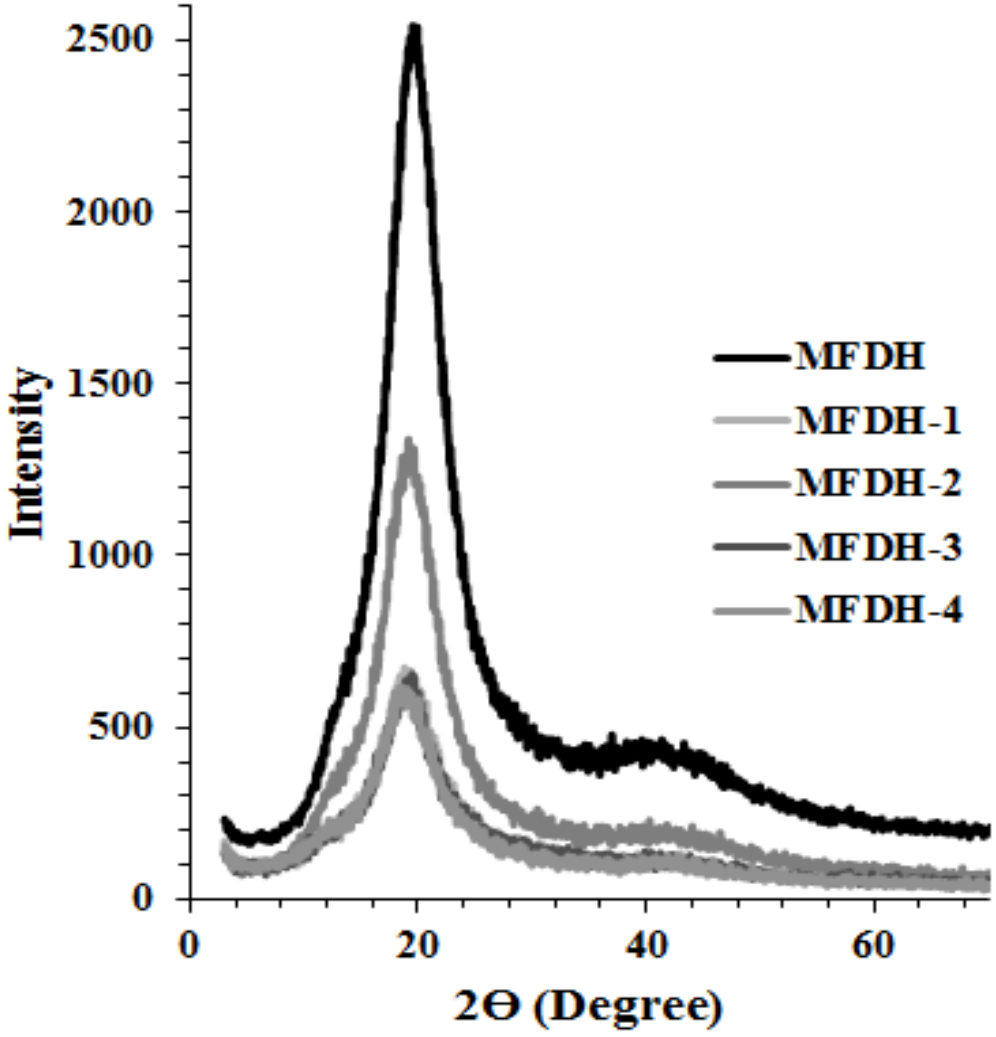


Figure 2.5 XRD patterns of the synthesized composites.

BET surface area results shown in Table 2.2 , showed the increase in the surface area as the CNT amount increased. Also, the BET adsorption isotherms showed that the composites are macroporous in nature as shown in Figure 2.6 .

Table 2.2 : Surface area of synthesized polymer/CNT composites

Composite	Surface area (m^2/g)
MFDH	3.6379
MFDH-1	8.5986
MFDH-2	10.2258
MFDH-3	12.3267
MFDH-4	17.8168

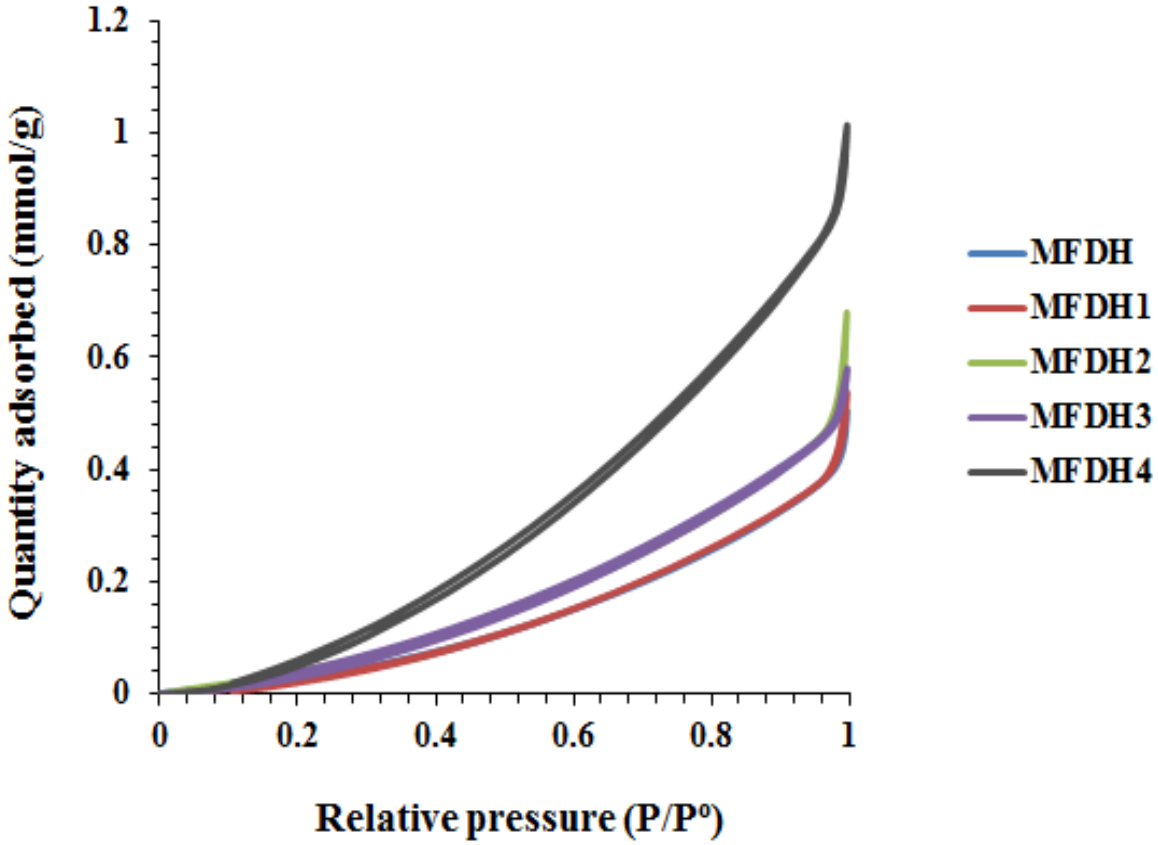


Figure 2.6 Adsorption/Desorption isotherms of the synthesized polymer/CNT composites.

Thermogravimetric Analysis (TGA) thermograms shown in Figure 2.7 revealed that the thermal stability of the synthesized polymer/CNT composites began to decompose at ~200^{o}C. The increase in CNT leads to a small decrease in the thermal stability; which could be attributed to the decrease in the semi-crystalline order of the polymer composites leading to lower thermal stability.

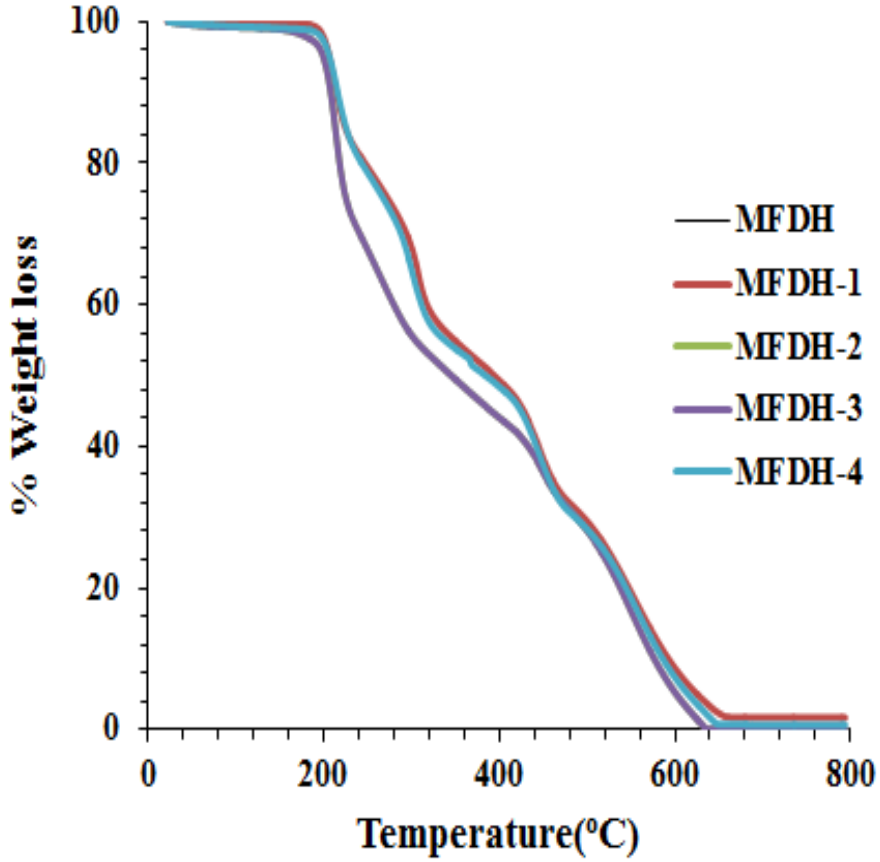


Figure 2.7 TGA thermograms of the synthesized polymer/CNT composites.

2.3.2 Result of factorial design

Based on the experimental design using MINITAB software, the adsorption tests were performed using the prepared polymer. The response removal was utilized to study the effect of the factors and their interactions. Figure 2.8 (a-c) depicts the normal plot, half normal plot and Pareto chart of the standardized effect. The factorial design results show that the initial concentration and temperature had the strongest effect on lead removal efficiency. Increasing the temperature increases the lead removal. The interaction between pH and the CNT:polymer had the highest interaction effect.

Figure 2.9 (a) indicates that the CNT: polymer with ratio of 0.05 had the highest adsorption efficiency among the three composites tested in these experiments. Decreasing the initial concentration and temperature and increasing the pH were found to increase lead removal efficiency Figure 2.9 (b). The highest interaction effect is between CNT: polymer, pH and initial concentration. Based on the DOE results, the CNT: polymer with ratio of 0.05 was selected to be used in the following work under the obtained optimum conditions. Figure 2.9 (c) depicts the output of the response surface plot showing the effect of dosage and time and their mutual effect, which is obtained by plotting values of contact time and dosage ratio. It can be noticed the effect of the contact time is more pronounced at low dosage than at higher dosages of the adsorbent.

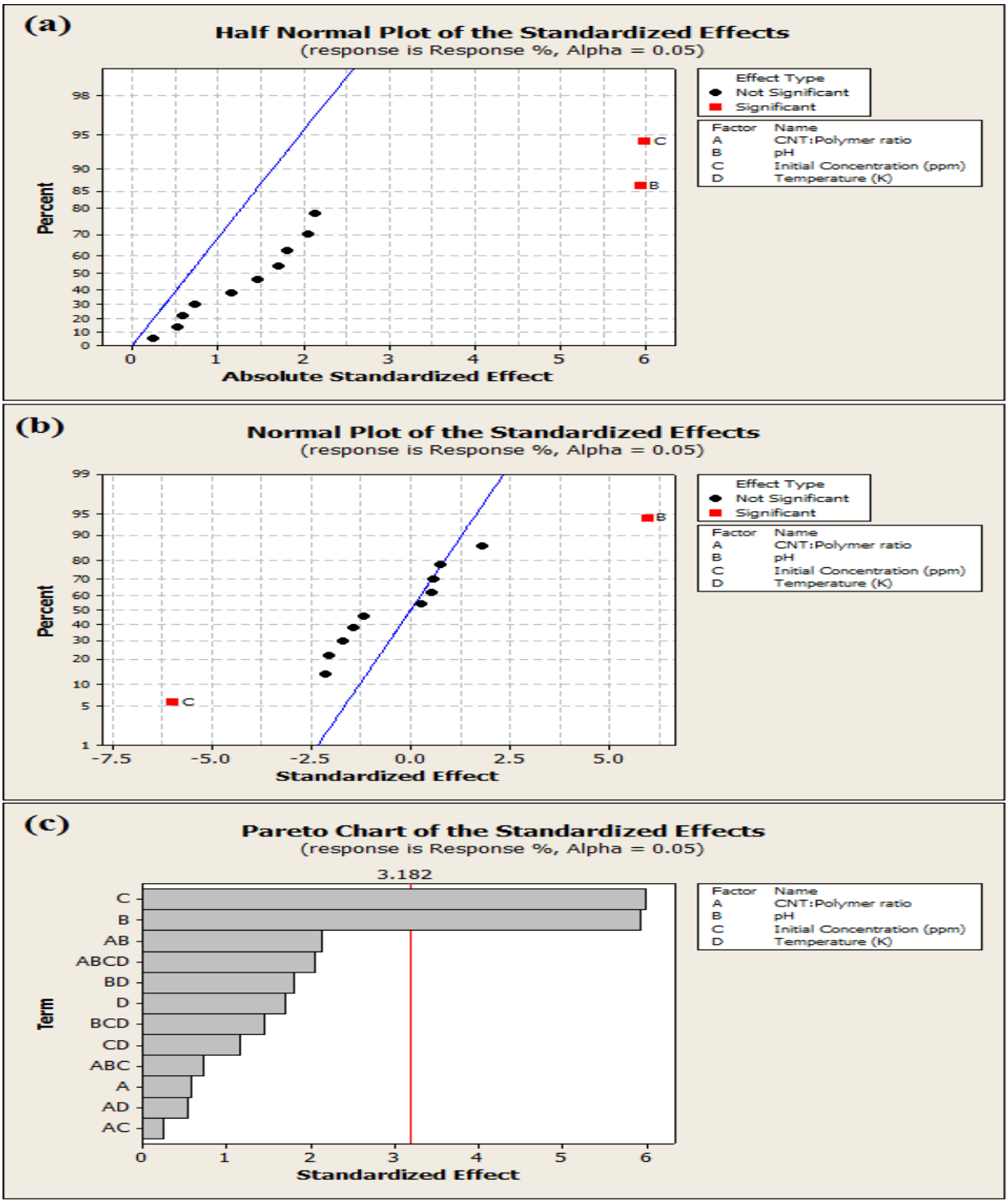


Figure 2.8 The factorial design plots showing (a) Normal plot (b) half-normal plot and (c) Pareto chart

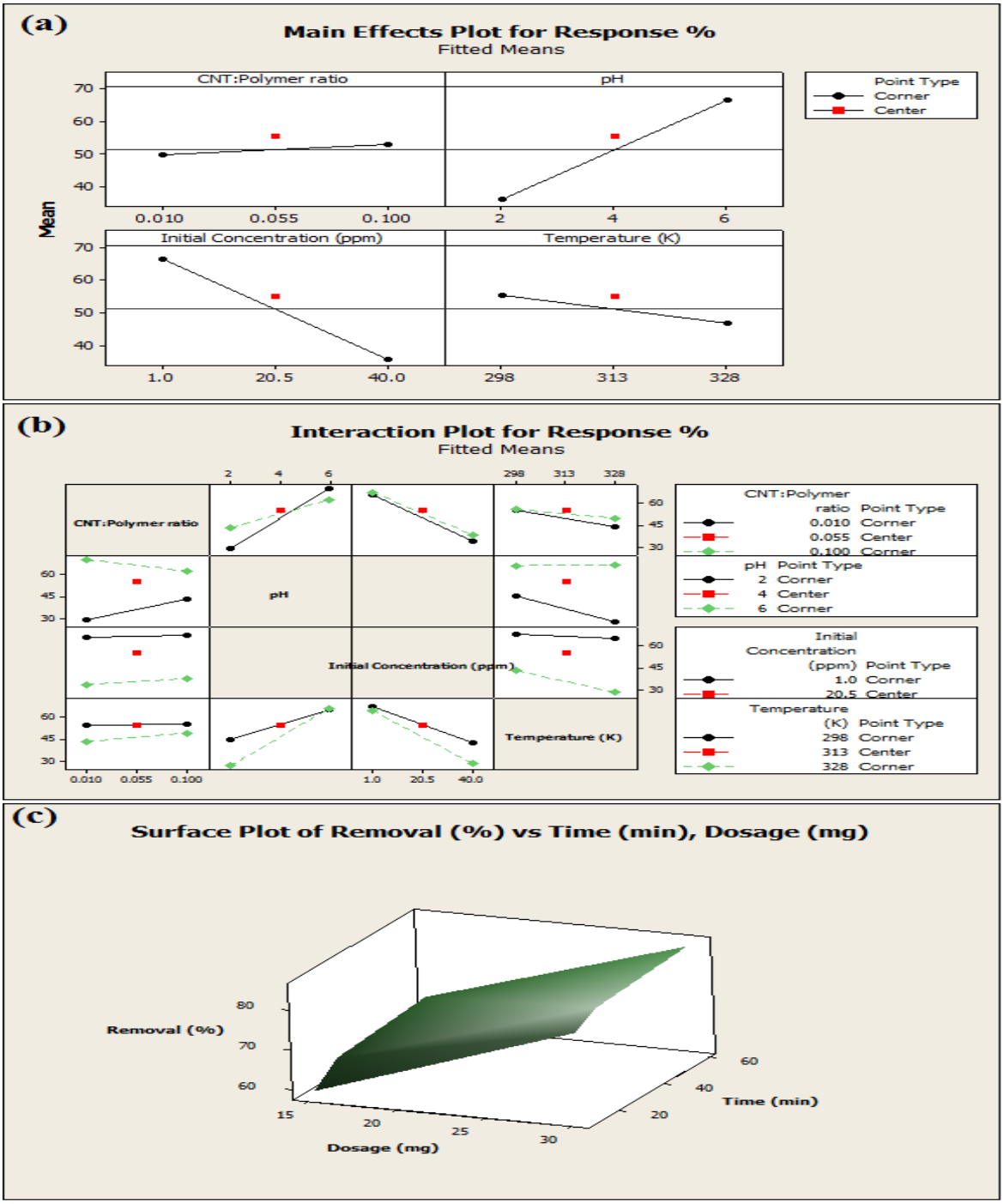


Figure 2.9 The factorial design plots showing (a) Main effect plot (b) Interaction plot ; (c) Response surface plot showing the effect of contact time and dosage and their mutual effect on the removal of lead.

2.4 Waste water treatment

In order to evaluate the real adsorption potential of the synthesized composites, a sample of industrial wastewater spiked with lead ions was treated with MFDH-3 which resulted in the best adsorption removal results Table 2.3 below. Treatment of a wastewater sample revealed the efficacy of MFDH-3 in the applicability to remove ~99 % of lead ions. The treatment of the waste water sample proved the potent usage of MFDH-3 as an industrial adsorbent for wastewater treatment.

Table 2.3 : Spiked industrial waste water sample treated with MFDH-3

Metal ion	Before treatment (µg/L)	After treatment (µg/L)
Pb	2869 ± 0.438	39.28 ± 0.438
Cd	0.71 ± 0.213	0.077 ± 0.213
As	102.5 ± 7.077	15.89 ± 7.077
Zn	< MDL	< MDL
Cu	32.18 ± 9.235	0.302 ± 9.235
Ni	40.88 ± 4.275	13.52 ± 4.275
Co	2.743 ± 0.405	0.878 ± 0.405
Mn	7.046 ± 1.215	7.707 ± 1.215
Cr	127.6 ± 3.594	22.26 ± 3.594

Mean and standard deviation of three replicates (n = 3). ± Values are the method detection limit (MDL), 3σ of the blank sample.

2.5 Conclusion

A novel series on Melamine based cross-linked polyamines/CNT composites have been synthesized, the results revealed that MFDH-3 (0.05% CNT) had the highest efficiency in the removal of lead ions from aqueous solutions. A sample of industrial wastewater spiked with lead ions was treated with MFDH-3 and the composite proved its high capability in the removal of wastewater providing evidence as a high potent adsorbent for industrial wastewater treatment.

CHAPTER 3

Synthesis of new cross-linked CNT functionalized melamine-alkyldiamines polymers for removal of toxic metal ions

ABSTRACT

A novel series of polymer composites were synthesized by functionalizing chlorinated carbon nanotubes with polymers of melamine, paraformaldehyde and various alkyldiamines bearing alkyl groups of 6,8,10 and 12 chain lengths via a single step polymerization reaction in N, N-Dimethyl formamide at 90°C while maintaining a stirring rate of 360 revolutions per minute. The new series of polymer composites with 1,6 diaminohexane, 1,8 diaminooctane, 1,10 diaminodecane and 1,12 diaminododecane (CMA1, CMA2, CMA3 and CMA4 respectively) were fully characterized using ^{13}C-NMR, Fourier transform IR, Raman spectroscopy as well as evaluation of elemental analysis. The surface properties, crystallinity, composition and morphology was investigated using BET surface analysis, Atomic force microscopy, Powder X-ray diffraction experiment and scanning electron microscopy

3.1 Introduction

The prevalence of toxic metal ions in aqueous media has called for great attention. Over the past few years, significant efforts have been directed towards removal and limitation of the adverse potentials of these toxic metal ions. Heavy metals generally are

characterized by their relatively high density of about 5g per cubic centimeter and high atomic weight. Heavy metals when present above a particular threshold value have been adjudged to be injurious to human health, aquatic organisms and the entire ecosystem as a result of their non-biodegradability, constant bio accumulation in vital body organs and selective interference with general body metabolism. Heavy metals contamination to a very large extent are responsible for endocrine disruption, anemia, diarrhea, fever, skin damages in humans; stunted growth, yellowish leaves , dead cells and under production of chlorophyll for photosynthesis in plants [10, 13, 66, 67, 80]. The contamination of the environment by toxic metal ions is brought about by industrial activities, metal refining, batteries production, pharmaceuticals etc. The crude technologies and traditional approaches employed by the industrial dispensation led to the release of toxic metal ions into the air, soil and water courses [16, 97-101].

Critical amongst these toxic metal ions is cadmium (Cd^{2+}) particularly dangerous because of its instant bioaccumulation in the human kidney as well as it long half-life period of about 9 to 35 years. Thus, cadmium ions stay long in the human system causing severe disruption of normal body metabolism and functioning [102, 103]. In the light of the adverse effects of the presence of cadmium ions, advances have been made to achieve viable and efficient technologies aimed at the removal of these toxic ions from contaminated water bodies and drinking water. These various approaches that been employed are ion flotation and exchange[67], reverse osmosis [74], chemical treatment and precipitation[1], solvent extraction , electrochemical treatment[66, 81] and adsorption [5, 6, 8, 70, 102]. Of all these recent advances in toxic metal ions removal technologies,

adsorption which involves the use of polymers, membranes, resins, activated carbon, fly ash and nanomaterials have proven to be one of the best options because of it efficiency, cost friendliness, ease of modification and subsequent reuse after regeneration without losing its high sorption potential [13, 70, 85]. Particular classes of these polymeric materials are polymers of melamine, paraformaldehyde and alkyldiamines because of their good sorption activity, ability to form chelates and ion exchange potential. This is due to the presence of active amine and carbonyl functional moieties [92, 93, 95, 96]. With all these advantages, these class of polymers still suffer from relatively surface area, pore size and thermal stability ; to address this loophole, functionalizing these class of polymers with nanomaterials having high surface to volume ratio, mechanical and thermal strength has proven to be a comprehensive approach towards synthesizing efficient adsorbents [2, 79, 89, 96]. This paper highlights the synthesis and characterization of CNT functionalized melamine-paraformaldehyde-alkyldiamines polymers while varying the chain length of the alkyldiamine group. The series of polymers were characterized exclusively and their surface morphology investigated using scanning electron microscopy coupled with energy dispersive X-ray. Their efficiency and adsorption potential for the removal of toxic Cd^{2+} was investigated and analyzed.

3.2 Experimental section

3.2.1 Materials

Melamine, 1, 6-diaminohexane, 1,8-diaminooctane, 1,10-diaminodecane, 1,12-diaminododecane and paraformaldehyde were supplied by Fluka Chemie AG (Buchs,

Switzerland) and were subsequently used as received without further modification. N, N-Dimethyl formamide, Acetone and Methanol were supplied by Sigma-Aldrich, Germany. All other solvents and reagents employed were of analytical and standard grade.

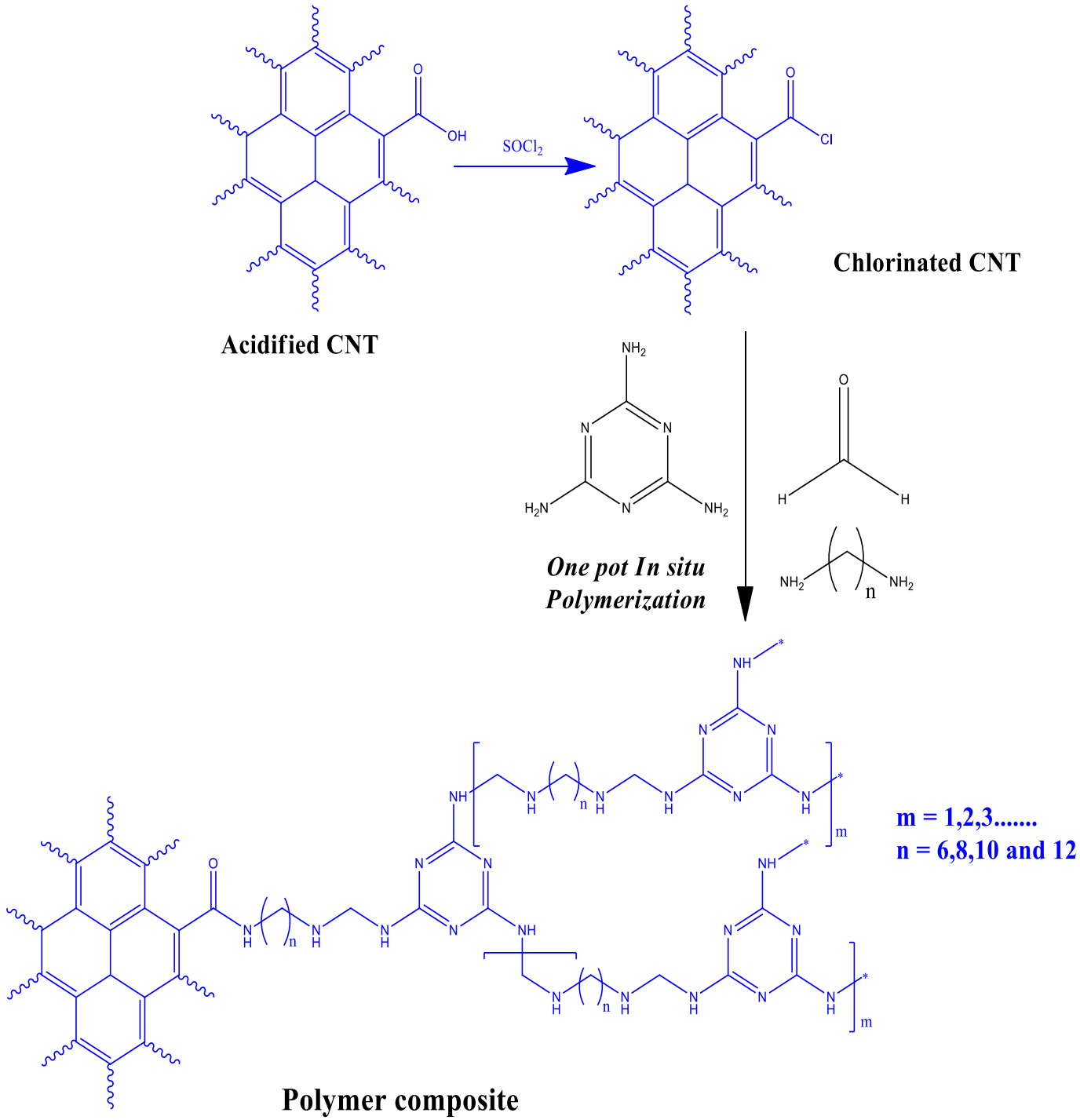
3.2.2 Chemical analysis, thermal analysis, morphology/surface characterization

Infrared spectra of the composites were analyzed on a Perkin Elmer 16F PC FTIR spectrometer using KBr pellets in the 4000-500 cm^{-1} wavelength region. Elemental analysis was done using a Perkin-Elmer Elemental Analyzer series II Model 2400. Powder X-ray Diffraction pattern for crystal nature was recorded using Rigaku Miniflex II Desktop X-ray Diffractometer with 3^0 and stop angle of 70^0 sampling step size of 0.03, scan speed 3.00, 30KV and 15mA. Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) analyses of the waste water before and after treatment with composites were done using ICP-MS XSeries-II (Thermo Scientific).

3.2.3 Synthesis of composites

Prior to the synthesis of the functionalized polymer composites, active chlorinated CNT was synthesized by reacting acidified CNT with thionyl chloride. Only 5% of the acidified CNT contained the acidic end (-COOH). Thionyl chloride was added in excess serving as an active chain end initiator and solvent (this reaction was carried out in a fume hood because thionyl chloride liberates hydrochloric gas when in contact with water. The polymer composites were prepared by reacting in a single step polymerization process melamine, 1, 6-diaminohexane and paraformaldehyde in the molar equivalent ratio of 1: 3: 6 respectively followed by substitution of 1,6-diaminohexane with 1,8-

diaminooctane, 1,10-diaminodecane, 1,12-diaminododecane to yield the remaining series while keeping constant 0.1 weight percent chlorinated CNT for all polymer composites. These reactions were carried out using 14-20ml of N, N-dimethyl formamide as solvent, under nitrogen atmosphere and were sonicated for 30 minutes for homogenization .The reaction was done using constant stirring of 360rpm, at a temperature of 90^0C for 24 hours. After complete polymerization has been achieved, the product was washed with distilled water five times to get rid of the DMF left in the product and thereafter washed with methanol three times to get rid of DMF, water, impurities and unreacted starting materials. The resultant was filtered using a vacuum pump and thereafter dried under vacuum at 60^0C for 12 hours until a constant weight was obtained.



Scheme 3.1 Reaction scheme for cross linked polymer/composite

3.3 Results and Discussions

3.3.1 Synthesis and characterization of cross-linked polymeric composites (CMA)

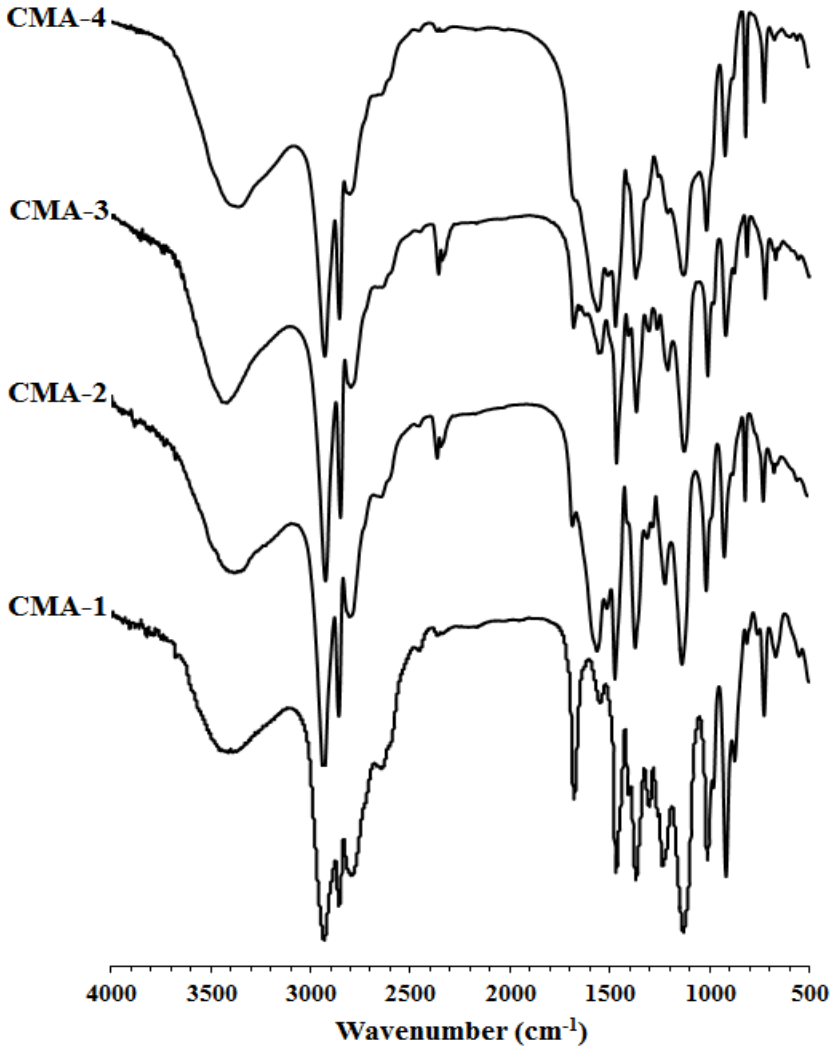


Figure 3.1 FTIR spectra of polymer composite

Figure 3.1 above shows the FT-IR spectra of the synthesized polymer composite which was consistent with the structure predicted by the reaction scheme. From the spectra, the broadband peak at around ~3450 cm^{-1} is assigned to the stretching vibrations of the NH_2 groups. The sharp stretching bands at ~1695 cm^{-1} and ~1472 cm^{-1} reflects the vibrations of the aromatic carbon carbon double bond (C=C). Also the sharp peaks at ~1585 cm^{-1} and ~1326 cm^{-1} is characteristic of carbon nanotubes, this is an indication that the polymer was completely functionalized by the carbon nanotubes. N-H wag vibration is represented by the band at ~760 cm^{-1} while the sharp peak at ~720 cm^{-1} indicates the CH_2 aliphatic chain of the polymer composite. Also, the highly pronounced sharp peaks at ~2905 cm^{-1} and ~2850 cm^{-1} can be assigned to the C-H symmetrical stretching of the diaminoalkane whose intensity increases as the aliphatic chain length increases.

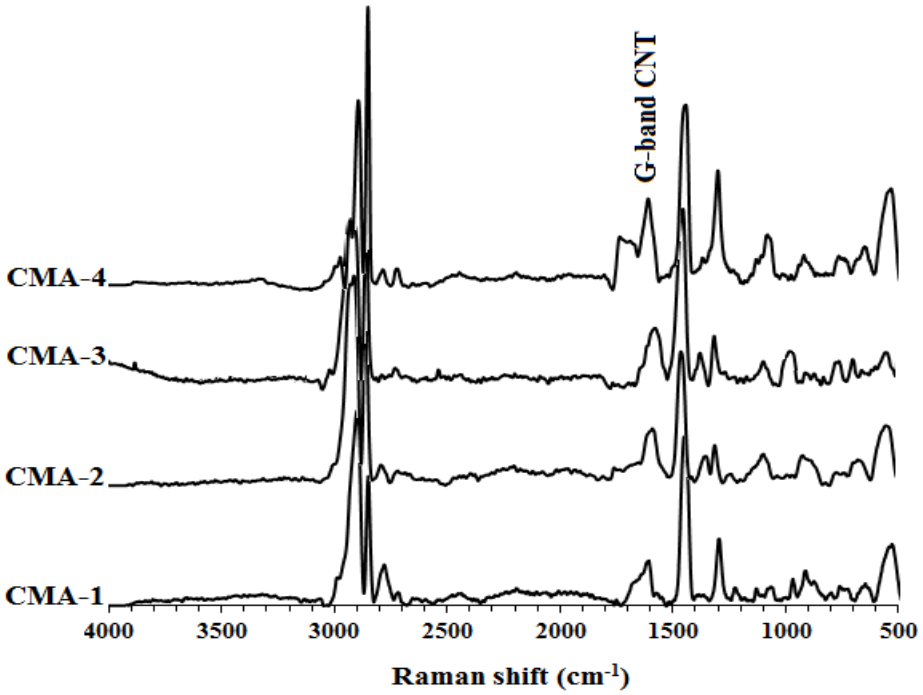


Figure 3.2 Raman Spectra of synthesized polymer composites.

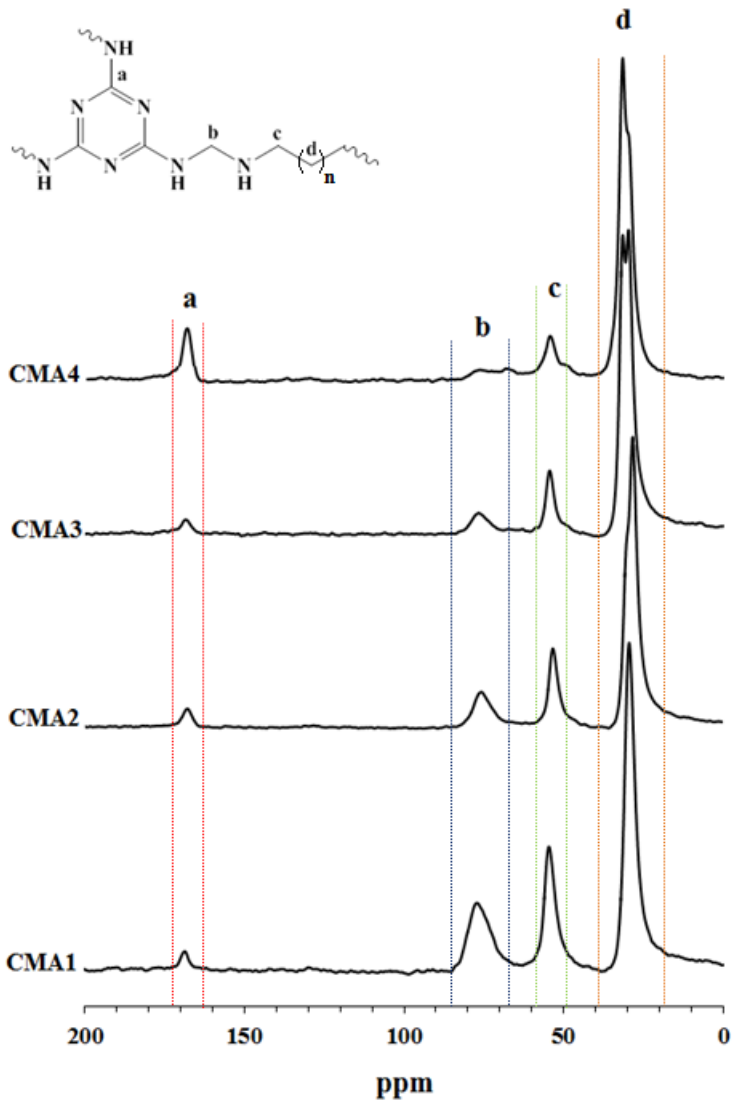


Figure 3.3 ^{13}C-NMR spectra of polymer composite

Solid state ^{13}C-NMR was employed to characterize the polymer as shown in Figure 3.3 above. The full description of the peaks and structure can be seen in the inset labeled structure. The result obtained was consistent with the reaction scheme predicted for the polymer composites.

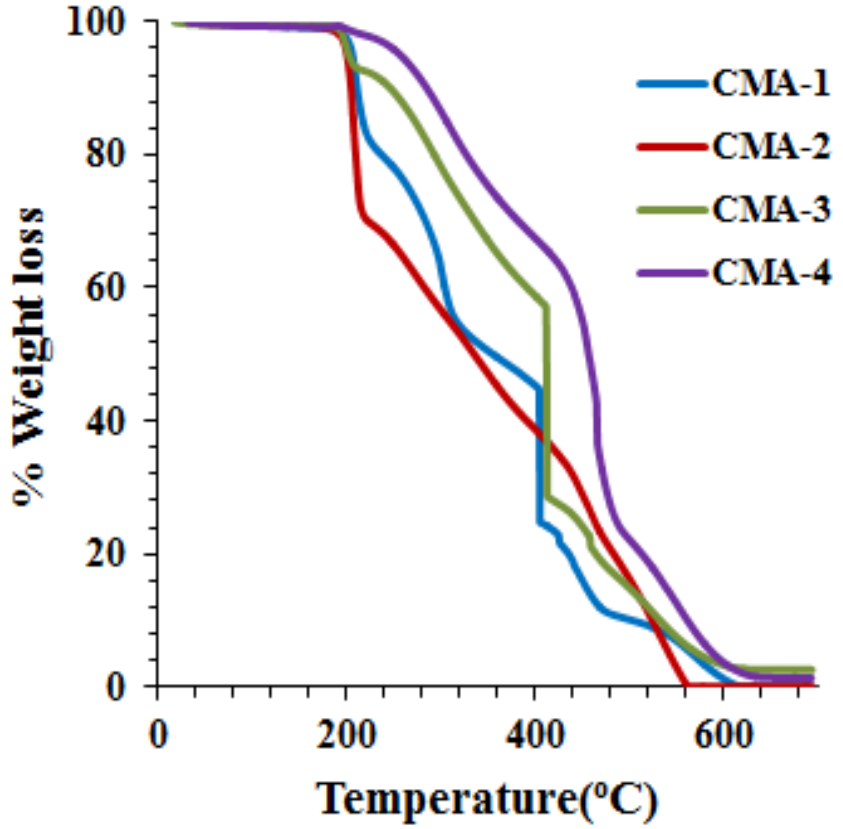


Figure 3.4 Thermo gravimetric analysis pattern of the polymer composites

The thermal stability of the polymer composite was investigated by thermogravimetric analysis as shown in Figure 3.4. There was a sharp depression which showed that the polymer composites were stable up to around 220°C. In addition there was an observed increase in thermal stability as we increase the chain length which can be quantitatively ascribed to the better packing as a result of increased aliphatic chain length.

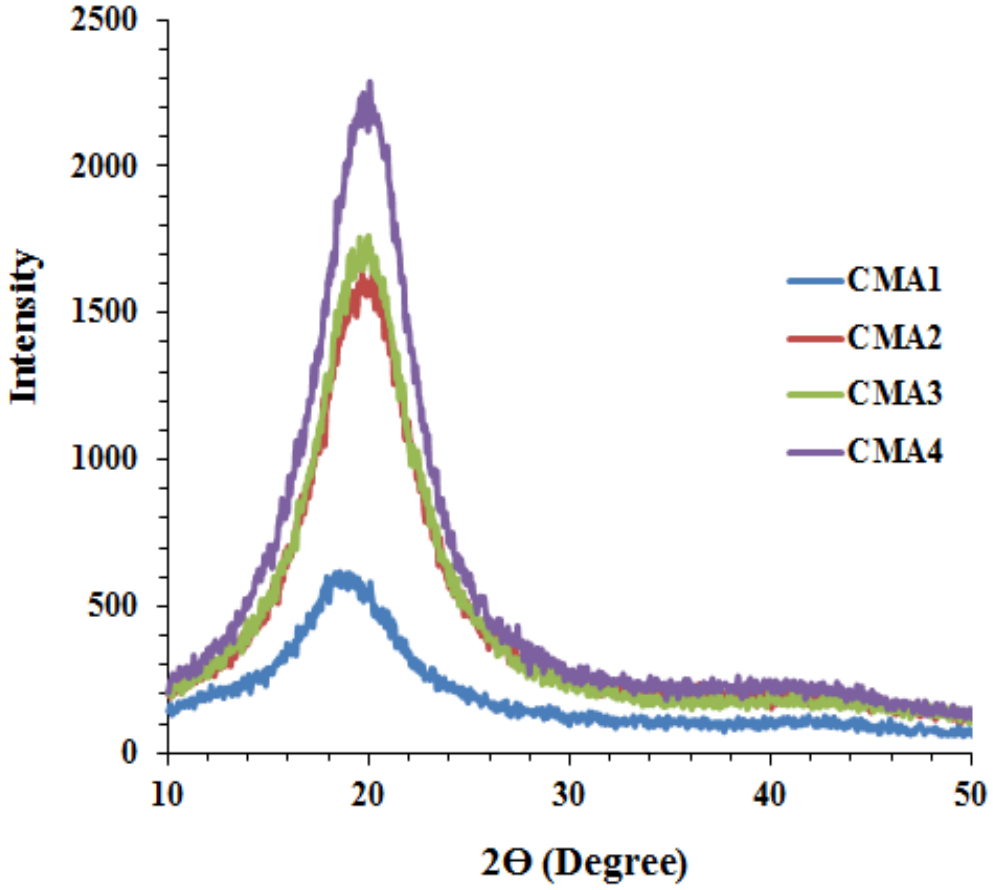


Figure 3.5 Powdered X-ray diffraction diagram for the polymer composite

The X-ray diffraction pattern was elucidated as shown in Figure 3.5 above, it shows a distinct peak at a 2Θ approximately 19° which indicates that the polymer composite has a crystalline nature. The crystallinity pattern observed increases as the chain length increases from 1,6-diaminohexane to 1,12-diaminododecane which bear more methylene groups which provides compactness and better packing.

3.3.2 Removal of Cadmium results

Effects of pH Aliphatic chain length

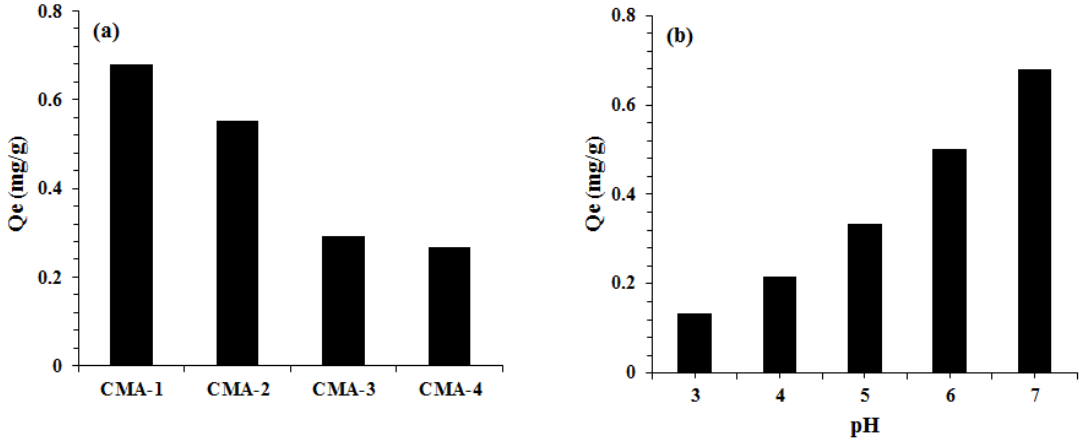


Figure 3.6 The effect of (a) chain length and (b) pH on adsorption capacity

From the figure above Figure 3.6 (a) , it can be concluded that increasing the chain length of the aliphatic chain will rather reduce the adsorption capacity; there the shorter the chain length, the better the adsorption capacity while maintaining a double amino active chain end. This can termed as a repulsion effect between the water loving hydrated shell of Cadmium (II) ions and the water repelling long interconnected methylene chain. Invariably, it better to keep the aliphatic chain length shorter in order to reduce the inactive methylene groups which creates bulkiness of the polymer composite without providing any significant sorption effect.

As illustrated in Figure 3.6 (b) above, increasing the pH of the solution towards neutral pH (pH = 7) increases the adsorption potential of the polymer composite. This was expected because at lower pH value which constitutes the acidic zone, there is high

prevalence of hydrogen ions (H^+) in solution which are known to compete with heavy metal ions for the active sites on the polymer composites, thereby limiting and reducing the availability of active adsorption sites for heavy metal sorption. In addition, as the pH value approaches 6 and above; the lead ions precipitate by forming lead hydroxides as precipitate by a metal speciation mechanism. This invariably frees up more active sites for adsorption, thus the increase in adsorption capacity as a function of increased pH is expected and valid. In addition, at a lower pH value, the ammonium ions becomes predominant in solution and repels positively charged Cadmium (II) due to its positive charge. On the other hand while approaching the neutral pH of 6 and above, the presence of hydroxyl ions (OH^-) initiates a form of electrostatic attraction with the Cadmium (II) ions thereby increasing the adsorption potential of the polymer composite

Effect of concentration

The effect of concentration was studied at pH of approximately 6 on prepared solutions of Cadmium (II) ions ranging from an initial concentration of 1mg/L to a final concentration of 5mg/L. The figurative expression of the effect of initial concentration on the adsorptive capacity of the synthesized polymer composite is shown in Figure 3.7 (a). It can be concluded that there is an increase in the adsorption potential of the adsorbent with the increase in initial concentration. To further buttress this adsorption mechanism, Freundlich and Langmuir isotherm models were used in order to investigate the adsorption parameters. Langmuir isotherm model, a tool for describing the nature of adsorption on a homogeneous surface in a single layer form was employed. Each active adsorption site can be effectively occupied by individual metal ions which are

independent of interactions with other adsorbed metal ions. The adsorption data obtained fit well as shown in Figure 3.7 (b), the Langmuir model described this in its linear form expressed as;

$$\frac{c_e}{q_e} = \frac{c_e}{Q_m} + \frac{1}{Q_m b} \quad (1)$$

Where C_e and q_e represents the concentration of the metal ions (mg/L) and the adsorption capacity at equilibrium respectively. b is the Langmuir constant related to the adsorption energy (L/mg) and Q_m is the maximum adsorption capacity measured in mg/g. There is a trend of higher adsorption as the concentration increases.

Freundlich isotherm model was used to investigate the process of adsorption that occurs on a heterogeneous surface of an adsorbent with uniform energy. The freundlich isotherm model can be expressed in its linear form as;

$$\text{Log } q_e = \log k_f + \frac{1}{n} \log C_e \quad (2)$$

Where $\frac{1}{n}$ and k_f are constants representing the intensity of adsorption and adsorption capacity respectively. As illustrated in Figure 3.7 (c), the linear plot shows that the data obtained fit the freundlich model. This is a clear indication that the adsorption process can be adjudged to be heterogeneous which high correlation coefficient value of 1 (R^2). The value $\frac{1}{n}$ predicts the heterogeneity of the surface with a value closer to zero indicating higher heterogeneity; thus the lower the value the favourable the adsorption of the cadmium ions. k_f value shows the binding affinity of cadmium to the polymer composite

surface and a higher value is relative to effective affinity. The values of Langmuir and freundlich isotherm models are presented in the table below.

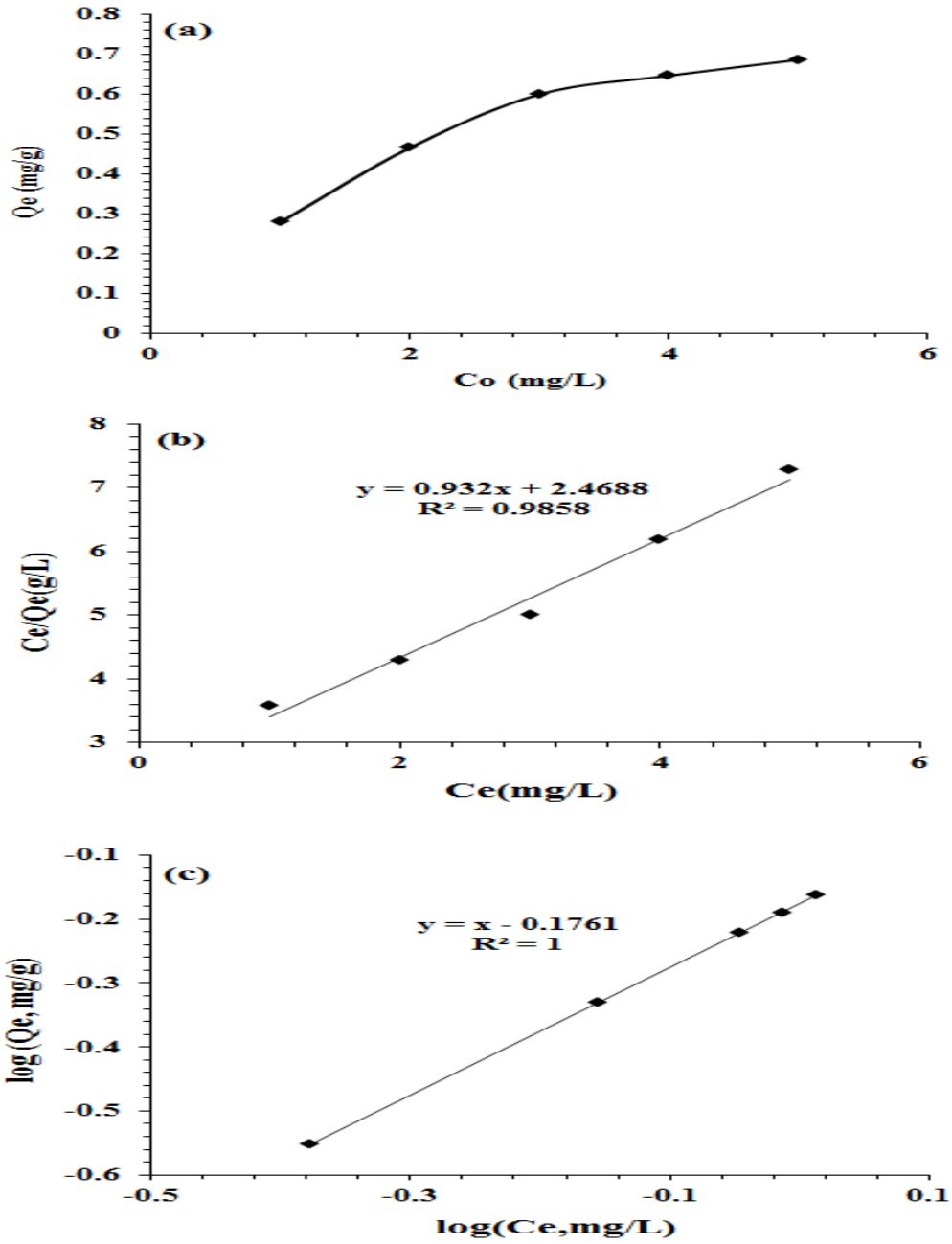


Figure 3.7 Graph showing (a) the effect of Cadmium (II) ion concentration on adsorption potential (b) Langmuir isotherm model (c) Freundlich isotherm model.

Table 3.1 Pseudo second order thermodynamics constant.

Polymer Composite	Langmuir Isotherm model			Freundlich Isotherm model		
	Q_m (mg g^{-1})	b (L mg^{-1})	R^2	k_f ($mg^{1-1/n}$ $g^{-1}L^{1/n}$)	n	R^2
CMA-1	1.0729	0.37751	0.9858	0.6666	1.0000	1.0000

Effect of time and kinetic model

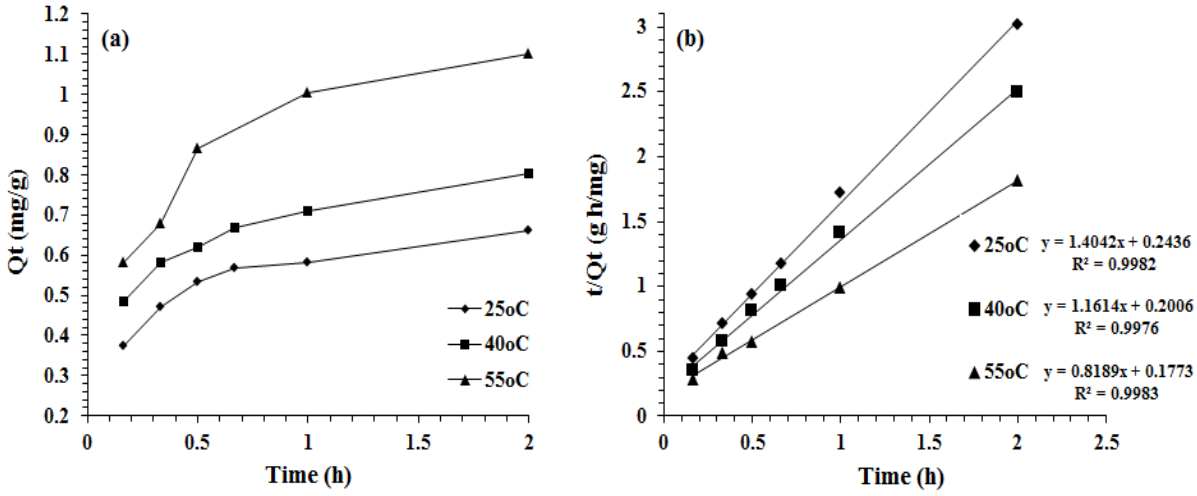


Figure 3.8 The effects of time on the kinetic models

From Figure 3.8(a) and (b) above, there is a positive effect of increase in adsorption capacity of the polymer composite as we increase the time of adsorption. This is an indication of more active surface pore sites active for cadmium (II) ion sorption, the availability of increased active sites can be credited to the large surface area bestowed on the adsorbent as a result of the presence of carbon nanotubes known for their high surface to volume ratio.

Pseudo second order kinetic model

Pseudo second order kinetic model based on adsorption at equilibrium was utilized for investigating the chemisorption pattern from aqueous solution; it is represented mathematically as;

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}\text{t} \qquad (3)$$

Where k_2 and q_e are the pseudo second order rate constant (g mg^{-1} h^{-1}) and capacity for adsorption at equilibrium respectively, and are both extrapolated from the slope and intercept of the graph in figure 8(b). The calculated adsorption capacity (q_e) matches the observed one and the fitness of the data to the pseudo order kinetic model indicates that the adsorption of the cadmium ions to the polymers composites may be by chemisorption.

Table 3.2 : Pseudo second order thermodynamics constant.

Temperature	Pseudo second order model				
(K)	$q_{e,cal}$ (mg g^{-1})	k_2 (g mg^{-1} h^{-1})	h (mg^{-1} g^{-1} h^{-1})	R^2	$q_{e,obv}$ (mg g^{-1})
298	0.7122	8.0932	4.1051	0.9982	0.7000
313	0.8610	6.7245	4.9850	0.9976	0.8300
328	1.2216	3.7794	5.6400	0.9983	1.1800

Effect of temperature and thermodynamic parameters

The effect of temperature as illustrated from the data extrapolated from the thermodynamics plot describes the direct relationship between the adsorption capacity and increasing temperature. As the temperature is increased, the adsorption capacity increases notably because of the expansion and widening of the pores of the polymer composite which allows for more capture and entrapment of cadmium (II) ions. This also points out that the adsorption mechanism is endothermic in nature as shown in Figure 3.9 (a) and (b). The thermodynamic parameters obtained are presented in table 3.3 below.

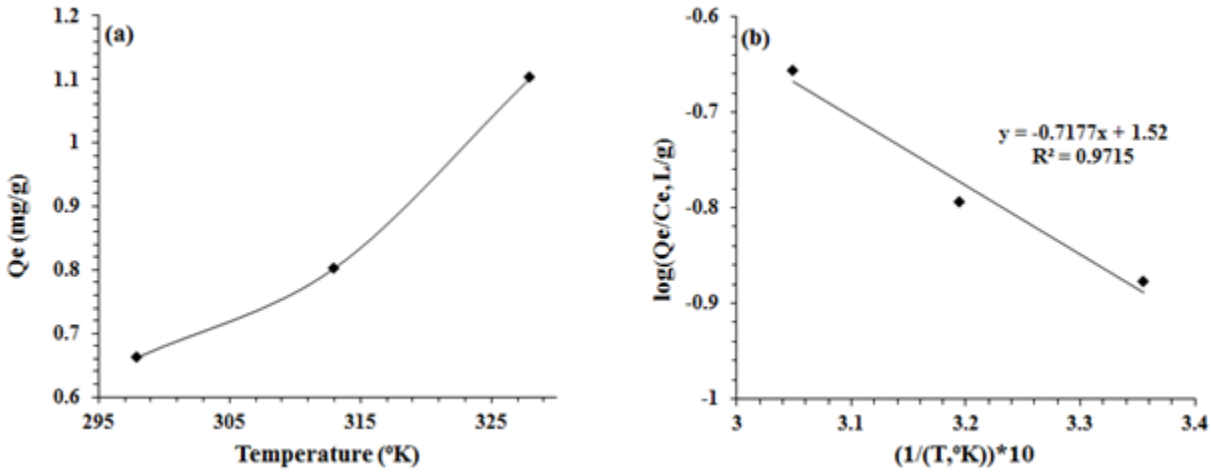


Figure 3.9 The effect of temperature on the thermodynamic model

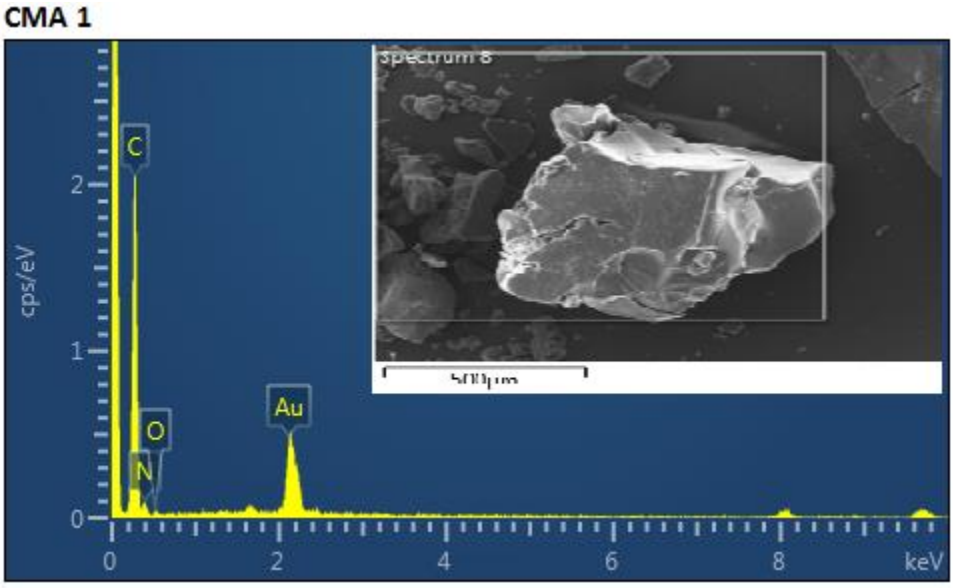
Table 3.3 Thermodynamic data for Cadmium adsorption.

Metal ion	Temperature(K)	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS (J/mol)	R^2
Cd^{2+}	298 313 328	-5.069 -4.632 -4.195	13.7419	29.1036	0.9715

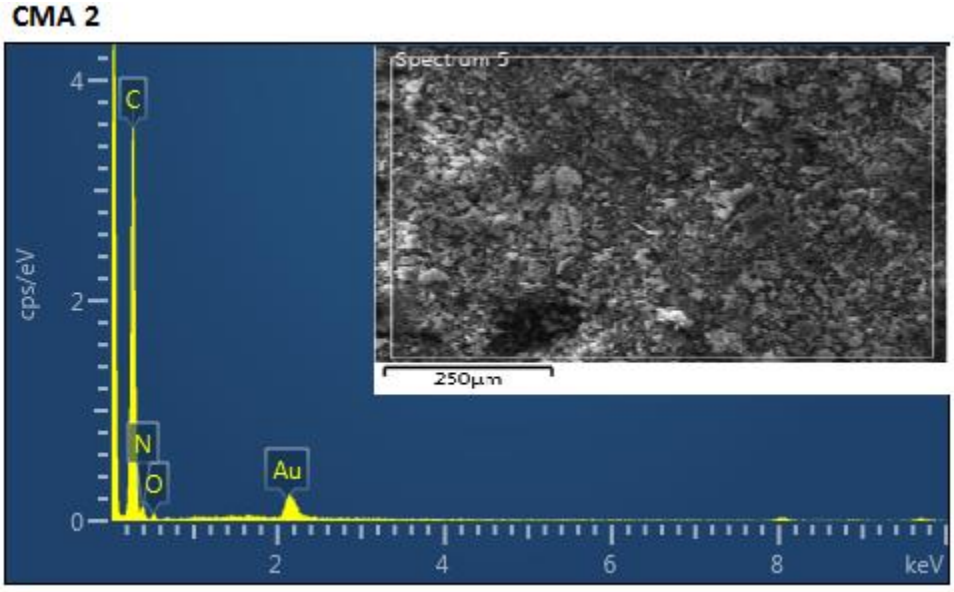
3.3.3 SEM – EDX images of CMA series

The polymer composites were characterized using SEM-EDX. The image revealed that the carbon nanotubes was evenly dispersed and incorporated into the polymer matrix as shown in fig 3.10 (a-d) while fig 3.10 (e) revealed the SEM-EDX image before and after cadmium removal using the best polymer composite (CMA1) earlier described. The smoothness of the image after cadmium removal is an indication that the cadmium was adsorbed on the surface of the polymer composite.

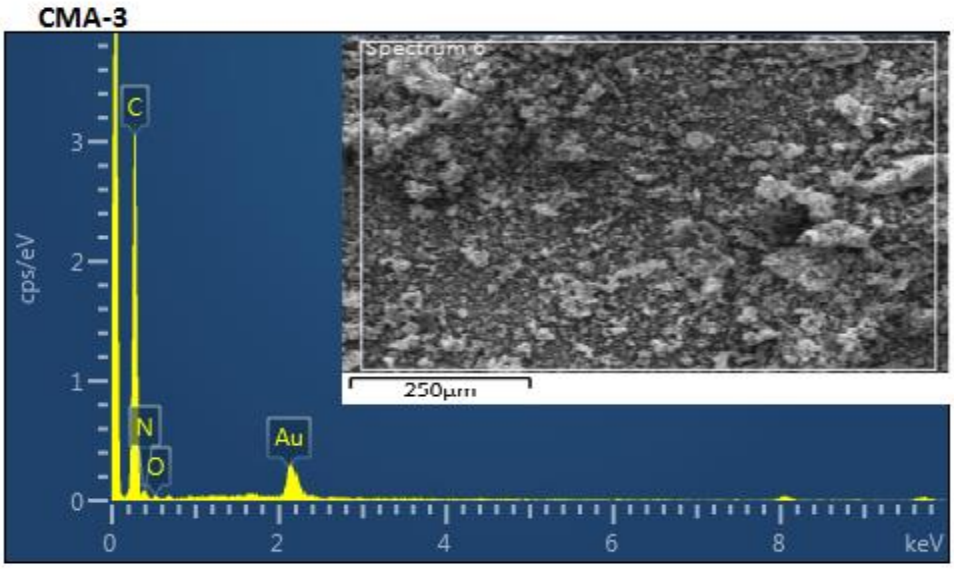
(a)


CMA 1
Spectrum 8
C
O
N
Au
cps/eV
keV

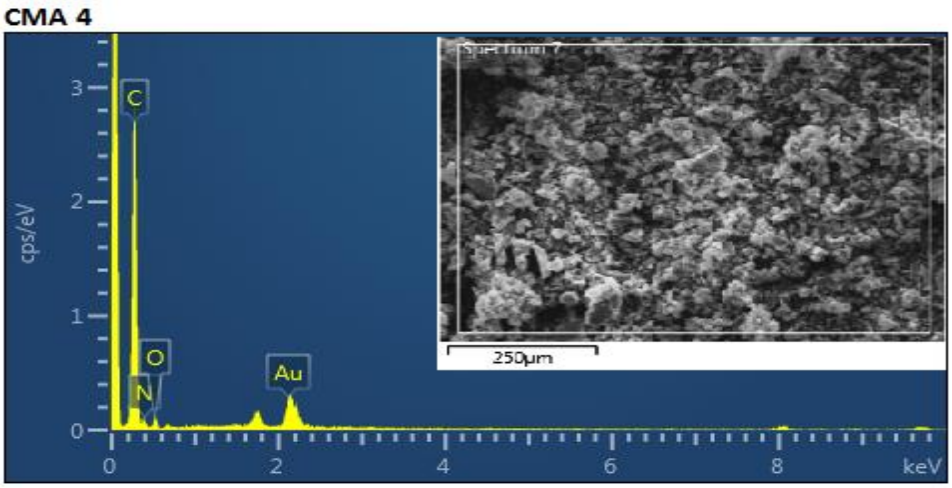
(b)


CMA 2
Spectrum 5
250µm
C
N
O
Au
cps/eV
keV

(c)


CMA-3
Spectrum 6
250µm
C
N
O
Au
cps/eV
0
1
2
3
0
2
4
6
8
keV

(d)


CMA 4
250µm
C
O
N
Au
cps/eV
0
1
2
3
0
2
4
6
8
keV

(e)

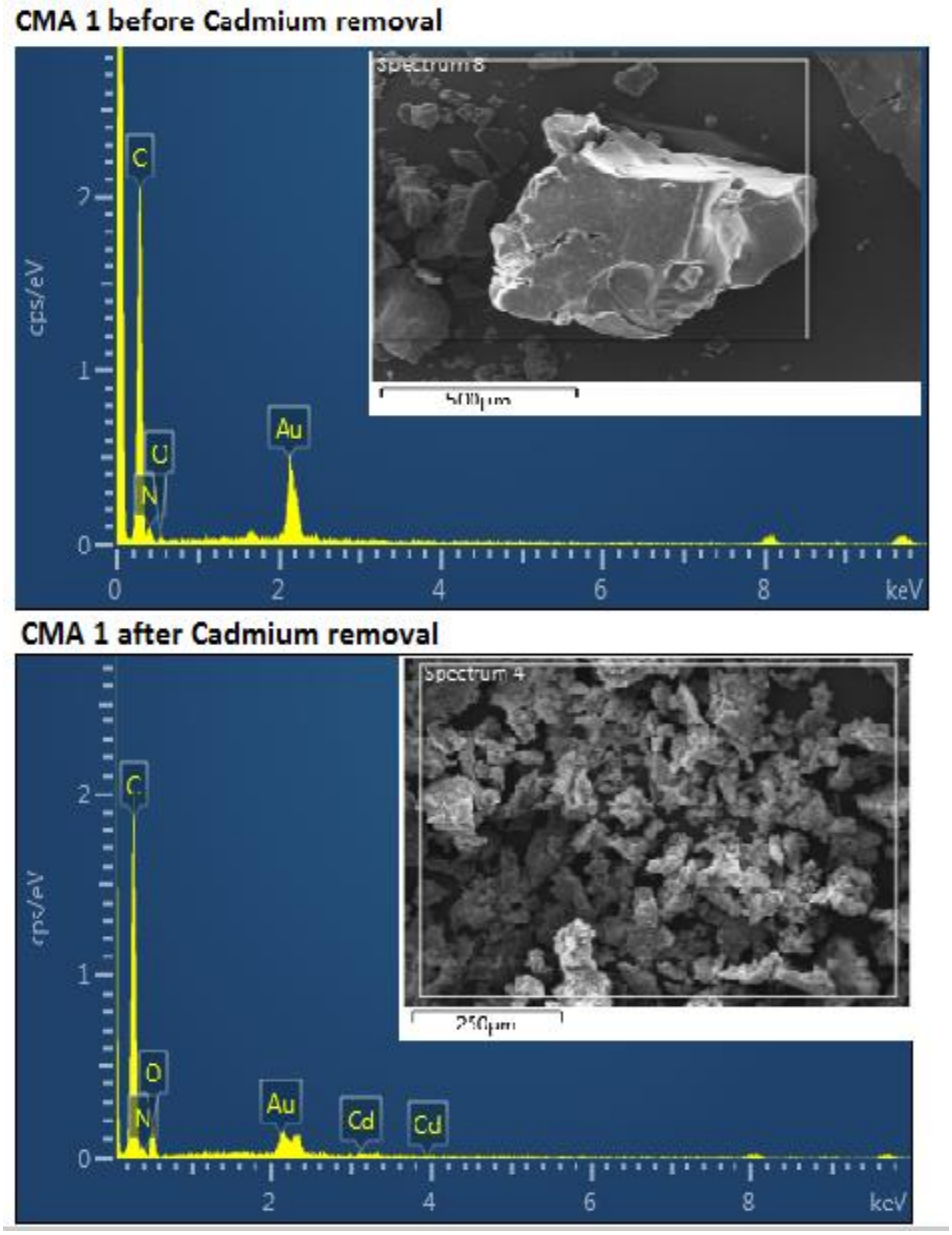


Figure 3.10 : SEM-EDX images of CMA 1, CMA 2, CMA 3 and CMA 4 (a-d), CMA 1 before and after cadmium removal (e).

3.3.4 Waste water treatment

Table 3.4 : Industrial waste water spiked and unspiked before and after treatment of CMA-1

Metal ion	Industrial waste		Industrial waste water spiked with cadmium	
	Before treatment	After treatment with CMA-1	Before treatment	After treatment with CMA-1
Pb	2690	0.654	0.654	0.463
Cd	0.687	0.871	3640	1678
As	95.32	23.37	95.32	21.83
Zn	0	0	0	0
Cu	20.07	18.16	21.13	13.92
Ni	39.38	20.8	38.46	18.65
Co	2.504	1.171	2.504	1.266
Mn	6.632	6.806	6.632	6.717
Cr	125.1	17.43	123.4	16.13

3.3.5 Conclusion

Carbon nanotubes functionalized polymer composites were synthesized; these new series of polymers were synthesized through a single step condensation reaction of melamine, paraformaldehyde and various diaminoalkanes while keeping the ratio of the carbon nanotubes constant. The structural, thermal and elemental properties of the synthesized polymer composite was elucidated and investigated. The polymer composite was used for the removal of cadmium (II) ions of various concentrations while optimizing the pH and time factors. It showed excellent adsorption potential both on spiked water sample and real industrial waste sample. The exceptional behavior of this polymer composite implies that the functionalization of polymers bearing active amino moieties with carbon nanotubes is effective for the removal of toxic heavy metal ions from waste water and aqueous solutions.

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- Novel Cross-Linked Melamine Based Polyamine/CNT Composite for Lead removal.
- Investigation of the effects of alkyldiamines chain lengths on the adsorption potential of Melamine based Polyamine/CNT composite for cadmium removal